

Article

Agronomic Effectiveness of Biochar–KCl Composites for Corn Cultivation in Tropical Soils

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Abstract: Potassium chloride (KCl) is the main source of potassium (K) in Brazilian agriculture, but its high import dependency and the need for split applications increase costs and expose the system to supply and efficiency risks. Understanding the availability and release kinetics of potassium (K) from biochar-based fertilizers (K-BBFs) is crucial for optimizing their use as full or partial substitutes for KCl in Brazilian agriculture. This study evaluated biochars derived from banana peel (BP), coffee husk (CH), and chicken manure (CM), both in their pure form and co-pyrolyzed with KCl (composites) at 300 °C and 650 °C, as K sources for corn grown in two contrasting Oxisols. For pure biochars, feedstock type and pyrolysis temperature significantly influenced K content and release kinetics. Higher pyrolysis temperatures increased K content in BP and CH biochars but not in CM, while also slowing K release in CH and CM. Co-pyrolysis with KCl increased biochar yield, ash content, and K availability. Composites released more K than pure biochar but less than KCl, and at a slower rate. Notably, banana peel biochar co-pyrolyzed with KCl at 650 °C (CBP650) exhibited 36% slower K release and reduced KCl use by 82% while maintaining similar K use efficiency and corn growth. All K-BBFs matched KCl in promoting robust corn growth in clay soil, increasing biomass by 5.3 times and K uptake by 9 times compared to unfertilized (no K addition) plants. In sandy Oxisol, K-BBFs boosted biomass by up to 3.5 times compared to unfertilized plants, though some pure biochars were less effective than KCl in supporting full corn growth. Soil texture strongly influenced K availability, with sandier soils exhibiting higher K levels in solution. These findings suggest that kinetic release studies in abiotic systems, such as lysimeters with sand, are not suitable for evaluating K-BBFs as slow-release fertilizers. Due to lower K retention in sandy soil and solution K levels exceeding 1100 mg L^{−1}, split applications of some K-BBFs are recommended to prevent corn cation uptake imbalances and soil K leaching. Additionally, granulating biochar–KCl composites may enhance K retention and regulate its release in sandy Oxisols.

Keywords: composites; co-pyrolysis; slow-release potassium fertilizers; K in soil solution; waste K recycling



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1. Introduction

Potassium is a nutrient required in large quantities by plants, ranking as the second most abundant element in plant tissue [1,2]. The highly weathered soils in Brazil have naturally low K availability, making crops grown in these soils heavily dependent on K fertilizers imported from foreign countries. In 2022, over 7.5 million tons of KCl were imported, significantly increasing food production costs [3,4]. Potassium chloride is mined in only a few countries and is highly soluble, with a high saline index and elevated Cl content,

which can potentially harm seed germination, crop growth, and development [5,6]. As a result, KCl requires splitting and careful application or, in some cases, replacement with alternative K sources that are chloride-free and offer improved agronomic effectiveness [7,8]. In recent years, research on alternative K sources in agriculture, such as biochar used alone or enriched with K fertilizers, has increased [9]. Biochar (BC) is a solid material produced through the pyrolysis of renewable organic wastes in the absence of oxygen [10,11]. Its properties depend on both the type of feedstock and the intensity of the pyrolysis conditions [12–15]. Thus, feedstock selection and pyrolysis temperature can be deliberately adjusted to achieve specific desired properties and K content in the final biochar [16–18]. Due to its diverse characteristics, BC is used to enhance ecosystem functions, including water filtration, greenhouse gas emission reduction, soil organic carbon storage, water retention, soil biota improvement, soil conditioning, and increased crop yields [19–23]. Some biochars also serve as nutrient sources, supplying essential elements such as N, P, and K to crops [24–26]. Consequently, research on the application of biochar for soil fertility improvement and its use as a fertilizer has expanded over the past two decades [27].

Among the alkali metals, K is typically the most abundant element in plant biomass. Its content can vary widely, ranging from 0.5 to 19 g kg^{−1} in common organic residues such as wood and sewage sludge to as high as 40–122 g kg^{−1} in algae and post-harvest food waste [28]. The ability of biochar to supply K to plants depends significantly on the feedstock type and pyrolysis temperature used in its production [29]. Understanding the K content and retention capacity of different feedstocks allows for the optimization of pyrolysis conditions to produce high-value biochar-based K fertilizers (K-BBFs). Pristine biochars often lack sufficient nutrient concentrations to serve effectively as fertilizers, as nutrients may be either inadequately concentrated, lost during pyrolysis, or released too slowly or inconsistently to meet crop demands. To address these challenges, various physical and chemical methods have been developed to enhance the agronomic value of biochars and their use as raw materials for fertilizer synthesis [30,31]. Feedstocks with higher K contents require lower pyrolysis temperatures for effective K concentration [32], while biomass with lower K contents can be enriched with KCl to produce fertilizers that can be applied at lower rates than raw biochars [28,33]. Identifying K-rich raw materials suitable for direct K-BBF production and integrating biochar with mineral K sources offer an environmentally sustainable and practical strategy for recycling K from waste materials generated in large quantities in Brazil. This approach not only enhances the agronomic effectiveness of mineral K fertilizers but also aligns with circular economy principles while providing the additional benefits of biochar application in agricultural soils [26,30].

Research indicates that potassium fertilizers derived from biochar can achieve equal or even superior efficiency in plant growth compared to mineral fertilizers [34]. Moreover, the potassium release from engineered biochars is slower than that from KCl [35–37]. For the development of these engineered biochars, it is recommended to employ physical and chemical techniques during both the pre- and post-production stages, such as co-pyrolysis, to enhance biochar properties and K content in the final composite. Co-pyrolysis is a process that combines two or more materials to obtain a composite whose technical performance, in a synergistic manner, overcomes its initial inputs. This process is carried out in the same industrial and lab apparatus as simple pyrolysis [16]. Among the benefits of co-pyrolysis, the improvement in the BC pore structure; the increase in heating value, biochar yield, and nutrient enrichment, including K content, in biochars; and the improvement in the control of nutrient release into the soil solution can be mentioned [38,39].

Research on K-rich feedstocks for the production of K-BBFs and the nutrient release dynamics of these fertilizers remains limited in Brazil. Furthermore, no studies have yet investigated the co-pyrolysis of feedstocks with high K content with KCl to produce a

fertilizer with a K content comparable to that of mineral K fertilizers (~50% K). Additionally, it remains unclear whether the resulting products, hereafter referred to as composites, can be classified as slow-release K fertilizers. These composites have the potential to combine the benefits of biochar with the readily available K from KCl, ensuring a balanced nutrient supply for plants. To explore this potential, banana peel (BP), coffee husk (CH), and chicken manure (CM) were selected as feedstocks for K-rich BBF production. These feedstocks were chosen based on their relatively high K content compared to those evaluated in previous studies, their widespread availability, and their role in promoting the valorization of Brazilian agricultural and organic wastes [40–44]. Their use contributes to sustainable waste management, enhances the value of agro-industrial byproducts containing K compounds, and allows the production of high agronomic value K fertilizers [45–47]. Corn (*Zea mays* L.) was selected as the test crop due to its global agricultural importance and its prominent role in Brazilian farming systems [48]. As one of the most widely cultivated crops in Brazil, corn has high potassium requirements and is highly responsive to K fertilization [49]. Optimizing K fertilization for corn is crucial not only for maximizing yield but also for reducing production costs, especially in regions with sandy soils and low K retention capacity [50].

Therefore, this study aimed to evaluate the potential of different K-rich biomasses (BP, CH, and CM), processed at two pyrolysis temperatures (300 and 650 °C), as well as their co-pyrolysis with KCl, for producing high-value K fertilizers. It also sought to investigate K release kinetics under controlled and soil-based conditions and assess the effectiveness of biochar–KCl composites in supplying K to corn grown in soils with contrasting textures and organic matter content. We hypothesized the following: (i) all K-BBFs would exhibit high agronomic value regardless of feedstock or temperature; (ii) higher pyrolysis temperatures would enhance K content and reduce the need for KCl in composites; (iii) K-BBFs would release K more slowly than KCl; (iv) some K-BBFs would match the agronomic performance of KCl; (v) K release dynamics would depend on soil texture.

2. Materials and Methods

2.1. Biochar Synthesis: Feedstocks and Pyrolysis Conditions

Banana peel (BP), coffee husk (CH), and chicken manure (CM) were collected from different locations in the city of Lavras (Minas Gerais State, Brazil) for biochar production. The collected feedstocks were dried in a forced-air circulation oven at 70 °C until they reached a constant weight, ground, and stored in covered containers for pyrolysis and further analysis of K contents. The K contents found in the feedstocks were as follows: BP 6.2%; CH, 2.6%; and CM 3.0%. For pyrolysis, the feedstocks were placed in stainless steel cylinders with lids, weighed, and then transferred to an electric muffle furnace equipped with a pyrolysis chamber and an automatic temperature sensor for slow pyrolysis. The heating rate was 10 °C min^{−1}, aiming to reach the target temperature (300 °C and 650 °C) which was maintained for 60 min. After pyrolysis, the biochars were cooled to room temperature, weighed to obtain the biochar yield, and then ground using an agate mortar and pestle, following the procedure adapted from Morais et al. (2023) [51]. The ground charred material passed through a 60-mesh sieve for the characterization analyses of the final biochars and synthesized composites. To unveil the capacity of the feedstocks to retain K after pyrolysis, the K retention of the pure biochars was calculated using Equation (1), adapted from Lang et al. [52].

$$\text{Biochar K Retention}(\%) = \frac{\text{K in biochar}(\%)}{\text{K in feedstock}(\%)} \times \text{biochar yield}(\%) \quad (1)$$

2.2. Co-Pyrolysis

In the co-pyrolysis stage, each feedstock was mixed with KCl to achieve a potential 50% K content in the final composite. The proportions of raw material and KCl were calculated based on the K retention in the composites (Equation (2)), adapted from Carneiro et al. [53]. The composites were also pyrolyzed under the same conditions as described in Section 2.1.

$$K \text{ retention} = \frac{K_{Comp} \times Yield_{Comp}}{(K_{BC} \times Yield_{BC}) + (K_{KCl} \times Yield_{KCl})} \quad (2)$$

where K and yield are the K content (%) and yield (%) of the composite, pure biochar, and KCl, respectively. The acronyms, pyrolysis temperatures, and proportions of K from the KCl and feedstocks of the formulated biochars and composites are shown and described in detail in Table 1.

Table 1. The acronyms and descriptions of the main features of the final biochars and produced K-BBFs.

Feedstock	Biochar Type	Pyrolysis Temperature (°C)	K from Feedstock (%)	K from KCl (%)	Acronym
Banana peel	Pure	300	100	0	BBP300
	Pure	650	100	0	BBP650
	Composite	300	60	40	CBP300
	Composite	650	82	18	CBP650
Coffee husk	Pure	300	100	0	BCH300
	Pure	650	100	0	BCH650
	Composite	300	65	35	CCH300
	Composite	650	78	22	CCH650
Chicken manure	Pure	300	100	0	BCM300
	Pure	650	100	0	BCM650
	Composite	300	45	55	CCM300
	Composite	650	57	43	CCM650

2.3. Characterization of Feedstocks, Biochars, and Composites

Electrical conductivity (EC) and pH were determined in a biochar–water suspension at a ratio of 1:10 (*w:v*). The suspension was first stirred for 60 min in a shaker table, left at rest for 30 min, and then analyzed using a Hanna HI2221 digital EC and pH meter [54]. Ash content was determined by placing 1 g of each sample in an open porcelain crucible in a muffle furnace at 750 °C for 6 h. The remaining mass after incineration was then weighed on a precision balance. For the total carbon (C) content analysis of the biochars and composites, we used an Elementar Vario TOC Cube automatic analyzer (dry combustion). The spectral signature, bands, and peaks related to functional groups in the biochars and composites were evaluated using Fourier transform infrared–attenuated total reflectance spectroscopy (ATR-FTIR) in an Agilent® Cary 630 spectrometer (Agilent, Santa Clara, CA, USA). This analysis and the ATR-FTIR spectra were generated in the wavelength range of 4000 to 650 cm^{−1} with a resolution of 4 cm^{−1}. The main peaks were identified and interpreted according to infrared libraries and assignments of spectral bands and peaks available in other studies for organic matrices and K fertilizers. The cation exchange capacity of the pure biochars and composites was determined following the methodology proposed by Lago et al. [55], which employs partial least squares regression (PLSR) in combination with Fourier transform infrared spectroscopy (FTIR). For the determination of total K content in BBFs, a total nitric–perchloric digestion was performed with the addition of catalysts (Na₂SO₄, CuSO₄, and Se). Potassium concentration in the digested extracts was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

2.4. Potassium Release Kinetics

Based on the total K content in the composites and pure biochars, a study of K release kinetics was conducted through sequential extractions of K eluted from sand samples with a 0.01 mol L^{-1} calcium chloride. For this purpose, mini-lysimeters were assembled, each containing a sample of biochar or composite mixed with sand (the sand was successively washed with acid solution and ultra-pure water) in three replicates [51]. A $0.45 \text{ }\mu\text{m}$ diameter pore filter was inserted between the top and bottom of the mini-lysimeter; above the filter, 2 cm of glass wool was added, followed by the biochar or composite–sand mixture, and finally, another layer of 2 cm of glass wool was added to reduce the impact of the K eluent solution directly on the fertilizers, as well as to prevent the preferential flow of CaCl_2 in the mini-lysimeter. The amount of biochar or composite added through the mixtures corresponded to 2000 mg of K, thus varying the mass of each biochar/composite placed in each mini-lysimeter. For the experiment, 100 mL of CaCl_2 solution was passed through each mini-lysimeter at each extraction time scheduled for the kinetics study, which were as follows: 0, 1, 2, 5, 12, 24, 96, 288, 480, and 672 h after the first extraction. Additionally, KCl was also placed in the mini-lysimeters as a positive control and pure washed sand served as the negative control (no K). Potassium content in the extracts was assessed using a flame photometer. After determining the K content in the extracts, the accumulated K was calculated after each evaluated time, and then the value was converted to the K release rate (%) according to Equation (3).

$$K \text{ release}(\%) = \left(\frac{K_t}{K_{t0}} \right) * 100 \quad (3)$$

where K_t is the accumulated K content at each evaluated time (mg kg^{-1}) and K_{t0} is the initial total K content (mg kg^{-1}) placed in each mini-lysimeter.

2.5. Agronomic Efficiency of Biochars and Composites

To assess the ability of the biochars to supply K to corn (*Zea mays* L.) plants, a greenhouse study was conducted using 2.7 dm^3 pots. The experiment was conducted in a greenhouse under natural light conditions. The average day-time temperature during the experiment was $35 \text{ }^\circ\text{C}$, night-time temperature was $20 \text{ }^\circ\text{C}$, and the mean relative humidity was 60%. Corn was cultivated in Red (RO) and Red-Yellow (RYO) Oxisols, which contrast in texture and organic matter (OM) content. Soils were collected from the 0 to 20 cm layer, dried, and sieved (2 mm), to obtain the air-dried fine earth (ADFE) which was used for the chemical analyses (Table 2). Soil acidity correction was performed to raise the base saturation to 70% [56], using CaCO_3 and MgCO_3 in a 4:1 ratio. Soils were mixed with carbonates and incubated for 30 days, maintaining moisture close to 60% of soil field capacity.

Among the biochars and composites, ten K sources were selected for the study of the agronomic efficiency of K fertilizers, as follows: BBP300, BBP650, CBP300, CBP650, BCH300, BCH650, CCH300, CCH650, BCM300, and CCM650. In addition to treatments with pure biochars and composites, KCl was added as a positive control (KCl), and a negative control (“No KCl”) was also tested. All treatments were arranged in a randomized block design in a greenhouse, with three replicates per treatment in each of the two contrasting tropical soils, totaling 72 pots. Potassium was added to soil samples at 400 mg kg^{-1} K, applied once at planting for biochars and composites and split into 4 applications for KCl. For the remaining nutrients, the corn plants were supplied with 400 mg kg^{-1} N, 50 mg kg^{-1} S, 20 mg kg^{-1} Zn, 5 mg kg^{-1} Mn, 4 mg kg^{-1} Cu, and 1.5 mg kg^{-1} B in both soils. Phosphorus was applied at a rate of 600 mg kg^{-1} for the Red Oxisol and 300 mg kg^{-1} for the Red-Yellow Oxisol. All the nutrients supplied to the corn plants were furnished as pure per analysis as

follows: NH_4NO_3 , NH_4HPO_4 , $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and H_3BO_3 .

Table 2. The characterization and main attributes of the Oxisols used in corn cultivation, under natural conditions (before liming and fertilization practices).

Soil	pH	K ⁺	Available P mg dm ^{−3}	Na ⁺	Ca ²⁺	Mg ²⁺ cmol _c dm ^{−3}	Al ³⁺ cmol _c dm ^{−3}	H + Al
Red Oxisol	4.5	31	0.1	3.0	0.3	0.2	0.6	7.2
Red-Yellow Oxisol	4.8	226	0.1	2.5	0.9	0.4	0.4	2.8
Soil	SB	eCEC cmol _c dm ^{−3}	CEC at pH 7	BS	m	Clay	Silt	Sand
				%			g kg ^{−1}	
Red Oxisol	0.6	1.2	7.8	7.7	50.0	620	160	220
Red-Yellow Oxisol	1.9	2.2	4.7	40.0	15.9	470	80	450
Soil	P-Rem mg L ^{−1}	OM dag kg ^{−1}	Zn	Fe	Mn mg dm ^{−3}	Cu	B	S-SO ₄ ^{2−}
Red Oxisol	16.6	3.7	0.3	50.6	3.4	1.1	0.1	2.5
Red-Yellow Oxisol	36.6	1.7	0.2	36.0	3.5	0.0	0.1	1.2

pH in water: 1:2.5 ratio. P, Na, K, Fe, Zn, Mn, Cu: determined with Mehlich-1 soil test. Ca, Mg, Al: extracted with 1 mol L^{−1} KCl. H + Al: extracted with SMP solution. SB: Sum of Bases. eCEC: effective cation exchange capacity at soil current pH. CEC at pH 7: cation exchange capacity at pH 7.0. BS: base saturation. m: Aluminum Saturation. OM, organic matter: determined by oxidation with Na₂Cr₂O₇ 4 mol L^{−1} + H₂SO₄ 10 mol L^{−1}. P-Rem: remaining Phosphorus content. B: boron, extracted with hot water. S: available S-sulfate extracted with Monocalcium Phosphate mixed with acetic acid.

After the initial fertilization, 10 corn seeds were sown, and soil moisture was maintained at approximately 60% of each soil's field capacity. After ten days of planting, thinning was performed, leaving two corn plants per pot. Nitrogen topdressing was performed at 10, 20, and 40 days after planting in all pots, and potassium chloride (KCl) was applied in the positive control. Soil solution samplers [57] were installed in all pots for soil solution collection at 1 (seed), 10 (V3), 20 (V6), and 50 (V12) days after planting to assess the levels of readily available K in the soil liquid phase. Approximately 10 mL of solution was extracted at each sampling time, and Ca, Mg, and K levels were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). All treatments and controls were tested in triplicate.

After 50 days of cultivation, the plants were harvested, dried in an oven at 60 °C until a constant weight was achieved, ground, and stored for subsequent chemical analyses. The dried biomass was weighed, and the samples were digested in a 4:1 mixture of nitric and perchloric acids. The potassium contents in the digested plant shoot extracts were determined using a flame photometer. Additionally, 30 g soil samples were collected from each experimental unit using a pot soil auger. These samples were then dried, sieved (2 mm), and stored for further analysis. The remaining (after corn cultivation) available K in the soil was extracted based on the Mehlich-1 soil test and quantified by flame spectrophotometry.

2.6. Statistical Analysis

For the characterization of K-BFFs, an analysis of variance (ANOVA) was performed for each variable, considering a three-way interaction model (feedstock × pyrolysis temperature × biochar type). When the three-way interaction was not significant, a new ANOVA model was applied, considering only two-way interactions. When the three-way interaction was significant ($p < 0.05$), the treatment means were compared using Duncan's multiple range test ($p < 0.05$), and the results are presented with treatment means, standard deviations, and statistical groupings. When the three-way interaction was not significant,

multiple comparisons were performed based on two-way interactions, with the results reported as treatment means and standard deviations.

The data of the K release kinetics were fitted to nonlinear mathematical models to adjust the amount of leached K from the lysimeters over time. The data were fitted to the following mathematical models: a linear model (Equation (4)), exponential model (Equation (5)), power function (Equation (6)), Elovich model (Equation (7)), Toth model (Equation (8)), and Gompertz model (Equation (9)).

$$K_t = a + bt \quad (4)$$

$$K_t = N_0 \exp(-kt) \quad (5)$$

$$K_t = at^b \quad (6)$$

$$K_t = a + b \exp(-ct) \quad (7)$$

$$K_t = \frac{at}{1 + bt^n} \quad (8)$$

$$K_t = a \exp[-e^{b-ct}] \quad (9)$$

where K_t is the amount of K released at time t . For the linear model, a is the initial amount of K released and b is the release rate constant over time. For the exponential model, N_0 is the maximum amount of K released during the kinetics study and k is the decay rate constant for K release. For the power function, a is the scaling coefficient and b is the exponent determining the rate of K release over time. For the Elovich model, a is the initial K content, b is the scaling coefficient, and c is the exponential decay rate constant. For the Toth model, a is the capacity-related coefficient, b is a constant that affects the curve shape, and n is the exponent related to the distribution of release sites over time. For the Gompertz model, a is the asymptote representing the maximum release, b controls the position of the inflection point, and c controls the growth rate of K release. These models were applied to describe the K release kinetics under the experimental conditions. The best mathematical model adjusted to each dataset was selected based on the highest coefficient of regression (R^2) values and the lowest root mean squared error (RMSE) and Akaike Information Criterion (AIC) values [51].

For the greenhouse experiment, Principal Component Analysis (PCA) was applied to identify patterns in the dataset and evaluate the effects of different K-BBFs on corn growth in two distinct tropical soil types. All statistical analyses were conducted using R (version 4.3.1), and the following packages: tidyverse (version 2.0.0), MASS (version 7.3.60), and multcomp (version 1.24.25) [58–62]. For the FTIR spectra plotting, normalization was conducted using Chemoface (version 1.66) [63].

3. Results and Discussion

3.1. Biochar and Composite Properties

The main properties of the biochars and composites (K-BBFs) produced in this work are shown in Table 3. These physicochemical characteristics are essential to understanding the behavior of each material as a potential potassium fertilizer, especially in relation to its nutrient content, release dynamics, and interaction with soil. Properties such as yield, ash content, total carbon, pH, electrical conductivity (EC), potassium content, functional groups (FTIR), and cation exchange capacity (CEC) were evaluated to compare the influence of feedstock type, pyrolysis temperature, and co-pyrolysis with KCl on the performance of the resulting K-BBFs.

Table 3. The main properties of the pure biochars and derived composites.

BBF	Biochar Yield	Ash (%)	C	pH		EC dS m ^{−1}	
BBP300	58.6	18.08 ± 0.59	54.9	9.44 ± 0.03	f	16.96 ± 0.03	e
BBP650	32.4	31.08 ± 1.13	55.3	9.97 ± 0.02	c	28.40 ± 0.52	d
CBP300	73.6	56.75 ± 7.69	30.7	7.95 ± 0.15	i	81.03 ± 1.27	b
CBP650	44.4	58.26 ± 0.52	39.2	9.63 ± 0.01	de	69.70 ± 4.74	c
BCH300	46.0	14.40 ± 0.26	66.4	10.11 ± 0.04	c	8.80 ± 0.19	f
BCH650	30.7	20.04 ± 0.52	71.2	9.71 ± 0.05	d	15.08 ± 0.04	e
CCH300	66.2	58.59 ± 0.40	34.8	7.93 ± 0.07	i	75.07 ± 3.12	c
CCH650	45.6	53.80 ± 0.61	39.9	9.56 ± 0.02	ef	72.97 ± 0.59	c
BCM300	69.2	47.56 ± 0.33	27.8	8.52 ± 0.04	g	7.20 ± 0.56	f
BCM650	55.4	61.09 ± 0.73	22.9	10.65 ± 0.02	a	7.40 ± 0.46	f
CCM300	86.4	79.51 ± 1.04	11.2	8.17 ± 0.24	h	87.37 ± 10.56	a
CCM650	73.8	82.96 ± 0.36	12.7	10.41 ± 0.02	b	86.17 ± 1.37	ab

The same letter indicates no significant difference among treatment means by Duncan's test at $p < 0.05$. EC: electrical conductivity; BBP: biochar of banana peel; CBP: composite of banana peel; BCH: biochar of coffee husk; CCH: composite of coffee husk; BCM: biochar of chicken manure; CCM: composite of chicken manure.

3.1.1. Yield

Regardless of the feedstock, the pure biochar yield decreased with rising pyrolysis temperature. Biochars derived from CM showed the highest yields, with a 20% decrease as the temperature was elevated to 650 °C. Next were the biochars from BP, which showed a 44% decrease in yield content with increasing pyrolysis temperature. Finally, the biochars from CH showed a 34% reduction as the temperature increased. The highest yield, observed for the chicken manure biochar, can be attributed to its high ash content, with values similar to those reported by Piash et al. (2021) [64], which is likely due to the elevated levels of inorganic compounds that accumulate in the matrix after the volatilization of C, O, N, S, and H compounds, as noted by Domingues et al. [43]. The decrease in all biochar yields with increasing temperature occurs due the thermal degradation of, and greater energy available to break, the strong organic bonds, and the greater volatilization of organic components as the charring conditions intensify [28]. This behavior has also been reported in previous studies using the same biomass types evaluated in this study [43,65]. Higher yields were observed for the composites compared to pure biochars, irrespective of the feedstock and pyrolysis temperature. This is probably due to the deposition of volatile compounds around the biochar caused by the addition of KCl [66]. Potassium chloride acted as a shield, in synergy with the feedstocks, preserving their organic matrix from thermal degradation. Furthermore, K has a positive impact on biochar production, since during the pyrolysis process there is an accumulation of alkali and alkaline earth metals in the biochar that contribute to the catalytic effect, increasing the biochar yield and also the ash content, with K having the greatest impact on the preservation of thermally derived biochar compared to Na, Ca, and Mg [67]. It should also be mentioned that KCl is less susceptible to thermal degradation than the feedstocks' constituents; thus, it is more prone to remaining in the final composite than organic compounds are.

3.1.2. Ash Content

The ash content was significantly influenced by feedstock, pyrolysis temperature, and biochar type, as well as their two-way interactions ($p < 0.05$). Increasing the pyrolysis temperature (650 °C) led to a higher ash content than at a lower temperature (300 °C). Regarding feedstock, chicken manure biochars had the highest ash content, followed by

banana peel and coffee husk, which formed distinct statistical groups ($p < 0.05$). The inorganic constituents present in CM biochar ash can act as flame retardants, reducing mass loss during pyrolysis and resulting in higher biochar yield [68]. A higher ash content in the waste derived from animal production systems compared to those of plant origins was also reported by Sarfaraz et al. [69], who found in their work an ash content of 72.6% for chicken litter. The composite biochars exhibited a significantly higher ash content compared to the pure biochars ($p < 0.05$). The interaction between biochar type and pyrolysis temperature showed that composite biochars produced at 650 °C had the highest ash content, while pure biochars at 300 °C had the lowest values. Additionally, the interaction between biochar type and feedstock indicated that chicken manure biochars consistently had higher ash contents, regardless of the biochar type.

3.1.3. Total Carbon Content

For the C content (Table 3) in pure biochars, an increase was observed with the rise in pyrolysis temperature for CH, which reached the highest C values (66% at 300 °C and 71% at 650 °C). In contrast, BP showed no difference in C content with increased pyrolysis temperature (55% at both 300 °C and 650 °C), which is relevant to adding it to soil C with a higher persistence rate. For CM, the relationship was reversed, with C content decreasing as temperature increased (28% at 300 °C and 23% at 650 °C). The increase in C content in CH biochars with increasing pyrolysis temperature may be due to a higher degree of polymerization, leading to a more condensed, aromatic C structure in the biochar matrix [70,71]. The lowest C contents in the CM biochars, and their decrease with increasing temperature, suggest that the organic compounds in this material are more prone to rapid loss with increased pyrolysis temperature before forming biochars with recalcitrant aromatic compounds; additionally, the inorganic matrix may experience relative enrichment over the organic matrix as charring conditions intensify [43]. The thermal degradation of C in carbonate forms is another explanation for the lower C content in animal wastes carbonized at high pyrolysis temperatures. Carbon content increased with the rise in temperature for all composites, which may be attributed to the higher proportion of feedstock used at 650 °C compared to 300 °C.

3.1.4. pH

The pH of the biochars was significantly influenced by the interaction between feedstock, pyrolysis temperature, and biochar type ($p < 0.05$), indicating that these factors act in combination to determine biochar alkalinity and liming value. Among the feedstocks, the chicken manure biochars had the highest pH values, followed by banana peel and coffee husk, which were significantly different from each other ($p < 0.05$). An increase in pH value (Table 3) was observed for pure biochars with increasing pyrolysis temperature for the BP and CM biochars, but this behavior was the opposite for the CH biochar. This increase can be related to the increase in ash content and the presence of minerals, such as carbonates (CaCO_3 and MgCO_3), as well as alkali elements, such as K, Ca, Mg and Na, mainly in the chicken manure feedstock [72,73]. The pyrolysis process distills the volatile and acidic components producing bio-oil or biogas while maintaining alkaline components, carbonates, and other salts in the ash biochar matrix [69]. The opposite behavior observed for the CH biochar may be due to its specific chemical composition. Enders et al. [74] demonstrated, in a study evaluating 94 types of biochars, that pH can vary widely and depends directly on ash content and pyrolysis temperature, offering an opportunity to adapt each biochar to specific agronomic applications. Nevertheless, the pH values in water of the pure biochars all showed an alkaline nature, since they ranged from 8 to 10.7. The composite biochars exhibited significantly higher pH values than the pure biochars

($p < 0.05$). Similarly, pyrolysis at 650 °C resulted in higher pH values compared to at 300 °C, regardless of feedstock. The interaction between biochar type and feedstock revealed that the composite biochars derived from chicken manure had the highest pH, whereas the pure biochars derived from coffee husk had the lowest pH. Additionally, the three-way interaction (feedstock $\times$ temperature $\times$ biochar type) confirmed that the composite chicken manure biochars processed at 650 °C exhibited the highest pH values, while the pure coffee husk biochars processed at 300 °C had the lowest pH values.

3.1.5. Electrical Conductivity (EC)

The electrical conductivity (EC), an indirect determination of the soluble salts present in a solution and able to conduct electricity, similar to pH, was significantly influenced by the interaction between feedstock, pyrolysis temperature, and biochar type ($p < 0.05$), indicating that the effects of these factors are interdependent. An increase was observed with the rise in pyrolysis temperature for the pure biochars. The composite biochars exhibited significantly higher EC values than the pure biochars ($p < 0.05$). Among the feedstocks, the chicken manure biochars consistently had the highest EC values, while the coffee husk biochars showed the lowest EC values across pyrolysis temperatures, results similar to those found by Domingues et al. [43]. The interaction between feedstock and biochar type revealed that the composite chicken manure biochars had the highest EC, whereas the pure coffee husk biochars had the lowest EC. The decrease in EC of the composites produced at 650 °C reflects the lower addition of KCl in the formulation of these composites compared to those formulated at 300 °C. These results highlight the importance of feedstock selection and biochar processing conditions, as higher pyrolysis temperatures and composite formulations generally led to increased EC levels.

3.1.6. Potassium Content

During the pyrolysis process, K in plant tissues and feedstock components is converted into plant-available K, which can then be returned to the soil as fertilizer [75]. The potassium content of the biochars was significantly affected by the interaction between feedstock, pyrolysis temperature, and biochar type ($p < 0.05$), indicating that the response of K levels depended on the combination of these factors (Figure 1). Within each type of feedstock, K levels can also vary among different types of organic wastes (animal and industrial origins, etc.), plant species, cultivation conditions, harvest timing, and even different parts of the plant residue analyzed [9]. As expected, the total K content in the pure biochars was directly dependent on the feedstock and pyrolysis temperature. This finding aligns with the research of Xiu et al. [75], which demonstrated that pyrolysis temperature is the most critical factor influencing K content in corn husk biochar. According to the authors, at pyrolysis temperatures ranging from 300 to 900 °C, the content and transformation process of the different forms of K in the biochar progress through three stages as the charring conditions intensify. Therefore, K tends to concentrate and be converted into highly soluble salts when the feedstock is pyrolyzed, unlike elements that can be volatilized, such as O, N, and S, or transformed into insoluble forms, such as the formed Mg salts [76]. However, the conversion of highly soluble K occurs up to a specific temperature. According to Biliás et al. [9], this threshold is 500 °C, where pyrolysis temperatures below this limit yield biochars with higher relative fractions of soluble K. In contrast, temperatures exceeding 500 °C promote the formation of insoluble K salts, particularly in biochars derived from feedstocks rich in aluminum or silicon compounds that are prone to interact and form K compounds of low solubility [9].

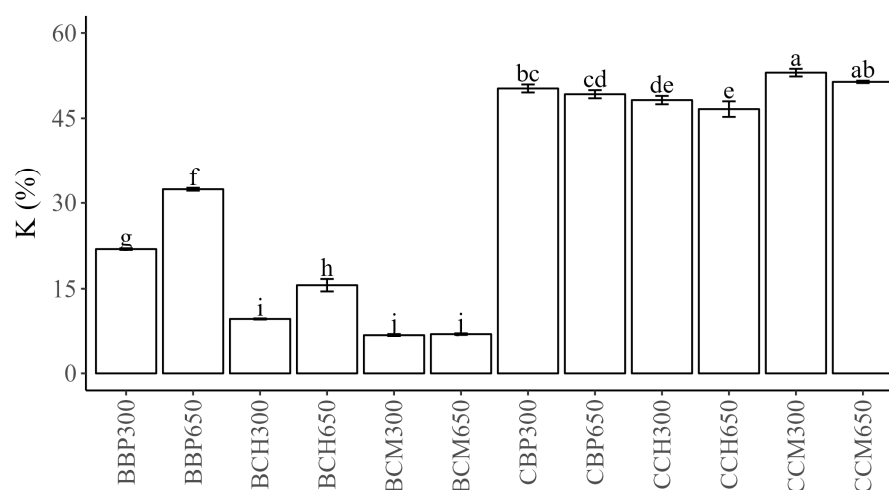


Figure 1. Total potassium (K) content (%) in pure biochars and composites. Means with same letters do not differ according to Duncan' test at $p < 0.05$. BBP: biochar banana peel; CBP: composite banana peel; BCH: biochar coffee husk; CCH: composite coffee husk; BCM: biochar chicken manure; CCM: composite chicken manure; 300 or 650 denotes pyrolysis temperature for biochar or composite.

The relationship between biochar K content and pyrolysis temperature is partially explained by the volatilization of organic compounds and the retention of inorganic ions such as K in the final biochar [28,77]. Among the studied feedstocks, the banana peel biochars exhibited the highest K content at both pyrolysis temperatures, with 22% at 300 °C and 32% at 650 °C, representing a 48% increase in total K content as temperature increased. A similar result was found by Bong et al. [78], who showed that increasing the pyrolysis temperature was the main factor affecting the potassium content of banana peel biochar. This was followed by CH, with K contents of 10% and 16% at 300 °C and 650 °C, respectively, showing a 60% increase. In contrast, CM maintained a relatively constant K content of approximately 7% at both temperatures, indicating no significant enrichment with increasing pyrolysis temperature. The lack of K accumulation in the CM-derived biochars under higher pyrolysis temperatures warrants further investigation. Additionally, potential K losses through volatilization as pyrolysis temperature rises should be explored in future studies. The K content in the BP biochars was significantly higher than that of the other feedstocks studied in this work, as well as biochars derived from other feedstocks reported in the literature [28]. Even at the lowest pyrolysis temperature (300 °C), BP biochar exhibited a high K content (22%), highlighting its strong potential for producing biochar-based K fertilizers. The composite biochars exhibited significantly higher K concentrations than the pure biochars ($p < 0.05$), aligning with the intended formulation goal of achieving a final K content of approximately 50%. The K content in the composite biochars ranged between 45% and 53%. Potassium retention (Equation (1)) is directly correlated with biochar yield. For the pure biochars, the K retention values were 207 and 169 for BBP300 and BBP650, respectively; 172 and 184 for BCH300 and BCH650; and 159 and 131 for BCM300 and BCM650. These results suggest that K losses or variations in biochar yield occur at different magnitudes depending on the feedstock and pyrolysis conditions.

3.1.7. FTIR Spectroscopy

The FTIR spectral signatures of biochars and their respective composites (Figure 2) revealed significant changes in infrared fingerprints as pyrolysis conditions intensified. Pyrolysis temperature plays a crucial role in shaping the structural and chemical composition of biochars, with higher temperatures promoting the thermal degradation of aliphatic groups and facilitating the formation of more condensed aromatic structures in

plant-derived biochars [79]. The biochars derived from BP (Figure 2a) and CH (Figure 2b) exhibited similar spectral signatures, with the slight differences likely attributed to variations in the lignin content of each feedstock [80]. In contrast, the biochars derived from CM (Figure 2c) displayed distinct spectral features, reflecting differences in ash content, mineral composition, and the potential resistance of specific organic functional groups and compounds in chicken manure to thermal degradation under increasing charring conditions. These findings emphasize the strong influence of feedstock composition and pyrolysis conditions on the chemical structure of the resulting biochars. They also highlight the importance of optimizing pyrolysis parameters to tailor biochar properties for specific applications.

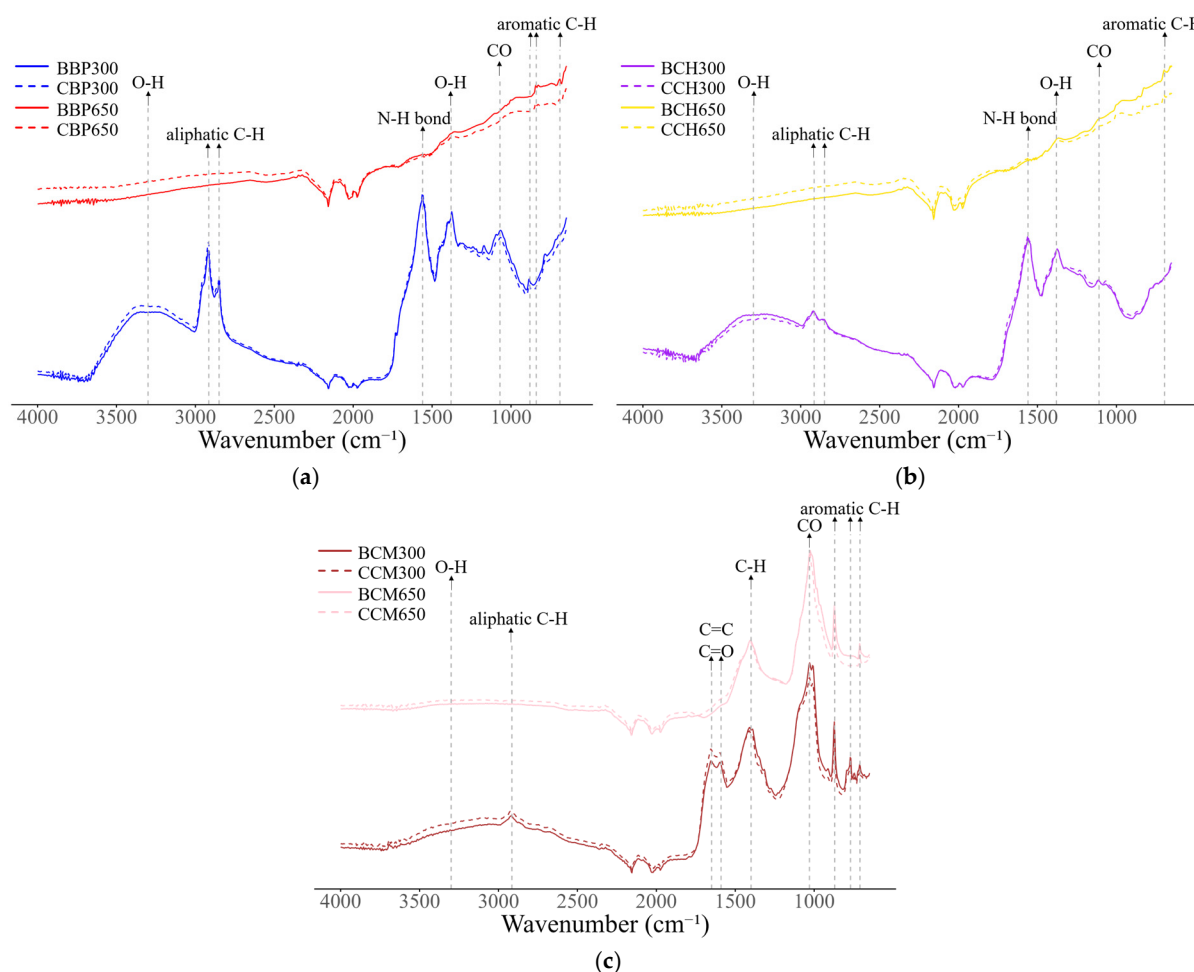


Figure 2. FTIR spectra of pure and composite biochars pyrolyzed at 300 °C and 650 °C. (a) Banana peel, (b) coffee husk, and (c) chicken manure. BBP: biochar banana peel; CBP: composite of banana peel biochar; BCH: biochar of coffee husk; CCH: composite of coffee husk biochar; BCM: biochar of chicken manure; CCM: composite of chicken manure.

In the biochars derived from BP and CH, aliphatic groups were detected at 300 °C, indicated by peaks in the 2915–2850 cm^{−1} region [43,81]. These peaks were absent in the biochars produced at 650 °C, suggesting the thermal degradation of organic radicals or the aromatic condensation of organic groups as temperature increased [73,75,80]. Similarly, the phenolic O–H bending (1310–1380 cm^{−1}) observed in the plant biochars charred at 300 °C disappeared at 650 °C, further supporting the formation of more condensed aromatic structures at elevated pyrolysis temperatures. In the region around 1560 cm^{−1}, the peaks observed in BP and CH biochars produced at 300 °C could be attributed to C=C stretching in aromatic rings, or possibly to amide (–CONH–) functional groups [54,82,83]. The removal

of volatile compounds during carbonization at higher temperatures results in the depletion of functional organic polar groups, leading to a subsequent reduction in a biochar's cation exchange capacity (CEC) [84]. In contrast, the chicken manure biochars exhibited distinct peaks at 1030 cm^{-1} even at higher pyrolysis temperatures, indicating the resistance of their pristine organic matrices to thermal degradation. This resilience is likely due to their high ash content, which may protect organic compounds during pyrolysis [43]. The peaks around 800 cm^{-1} in all the spectra suggest the presence of aromatic rings, which are particularly pronounced in CM biochars. Notably, the addition of KCl did not significantly alter the organic structure or spectral signature of the biochar composites, regardless of feedstock type or pyrolysis temperature.

3.1.8. Cation Exchange Capacity (CEC)

Cation exchange capacity (CEC) is a key factor in evaluating the potential of biochars for agricultural and environmental applications, as it significantly influences the retention of cationic nutrients, including K, in weathered soils [85]. As expected, the CEC values of the BBFs, estimated based on FTIR spectral data and mathematical equations, varied according to feedstock type and pyrolysis temperature (Table 4). The CEC values ranged from 24.4 to 63.1 for the pure biochars and composites formulated at $300\text{ }^{\circ}\text{C}$, and from 2.9 to 18.2 for those prepared at $650\text{ }^{\circ}\text{C}$. These values align with those reported in the literature [86]. The decrease in CEC with increasing pyrolysis temperature occurs because lower temperatures generally preserve oxygen-containing functional groups, while higher temperatures lead to the thermal degradation of these organic groups, reducing the final biochar's CEC [55]. The highest CEC values were observed for the banana peel biochars, likely due to the high potassium content of this biomass. During pyrolysis, potassium may intercalate and promote the separation of carbonaceous lamellae through the oxidation of cross-linking carbon atoms [85]. The incorporation of KCl in composite synthesis led to a reduction in CEC. In the composites produced at $300\text{ }^{\circ}\text{C}$, this reduction was relatively minor: 3.5% for BP, 0.8% for CH, and 7.8% for CM. However, in BBFs produced at $650\text{ }^{\circ}\text{C}$, the reduction was significantly more pronounced, reaching 44.4% for BP and 31.2% for CH. Interestingly, in the case of CM, the CEC increased with the addition of KCl in the composite produced at $650\text{ }^{\circ}\text{C}$.

Table 4. Predicted cation exchange capacity (CEC) of pure biochars and derived composites.

Charred Matrix	CEC ($\text{cmol}_c\text{ kg}^{-1}$)
BBP300	63.1
BBP650	15.4
BCH300	37.9
BCH650	18.2
BCM300	26.5
BCM650	2.9
CBP300	60.9
CBP650	8.6
CCH300	37.6
CCH650	12.5
CCM300	24.4
CCM650	3.2

BBP: biochar from banana peel; CBP: composite from banana peel; BCH: biochar from coffee husk; CCH: composite from coffee husk; BCM: biochar from chicken manure; CCM: composite from chicken manure. Numbers 350 and 650 indicate pyrolysis temperatures used in biochar and composite production.

3.2. Potassium Release Kinetics Results

Considering that the forms and availability of K in biochar can vary depending on the feedstock and pyrolysis temperature, it is essential to evaluate the release of K over time. This assessment helps determine the optimal conditions for achieving specific agronomic goals, aiding in applications such as recommending K fertilizers for crops. To understand the release dynamics of K from the BBFs, an experiment was conducted to simulate K release in a CaCl_2 solution over 28 days (Figure 3). The K release kinetics dataset was fitted to six mathematical models, and the most appropriate model for each biochar and composite, compared to KCl, was selected based on the highest regression coefficients (R^2) and the lowest root mean square errors (RMSE) and Akaike Information Criterion (AIC) values [51]. Detailed results for each model are presented in Table A1, Appendix A. Among the evaluated models, the Toth and Gompertz equations provided the best fit (high R^2). However, since the Toth equation accounts for the heterogeneous surface of biochar, leading to a nonlinear K release into the solution, it was chosen as the most suitable model for all the treatments to describe the K release from the BBFs over time.

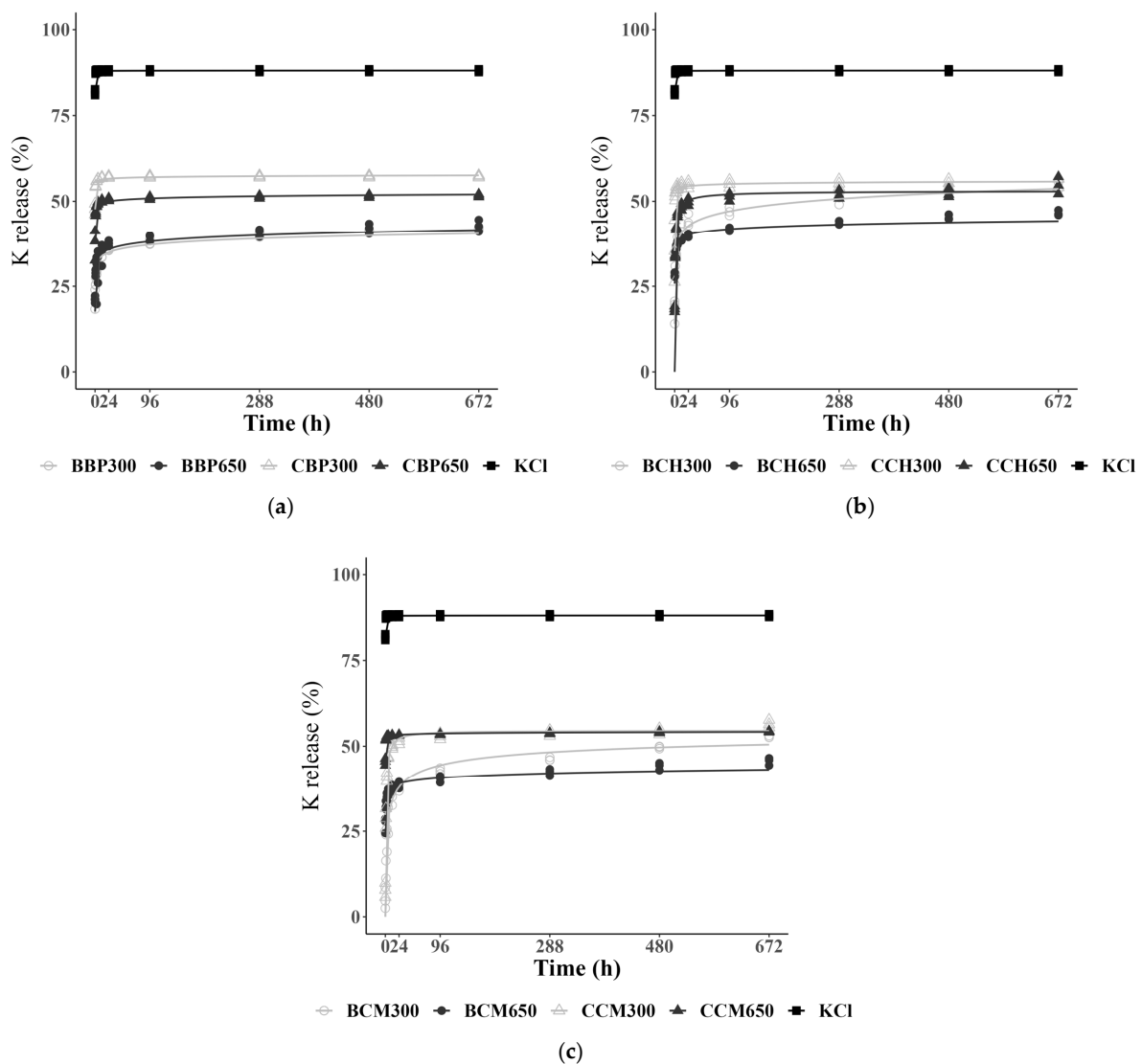


Figure 3. Release kinetics of K (%) in CaCl_2 over incubation time for pure and composite biochars compared to KCl: (a) banana peel biochars and composites, (b) coffee husk biochars and composites, (c) chicken manure biochars and composites. BBP: biochar banana peel; CBP: composite banana peel; BCH: biochar coffee husk; CCH: composite coffee husk; BCM: biochar chicken manure; CCM: composite chicken manure.

The release of K from K-BBFs (Figure 3) is a complex and non-homogeneous process, exhibiting variable release rates that do not follow a first-order reaction or a simple chemical mechanism [75]. A rapid K release was observed within the first 24 h, followed by a slower release phase, eventually reaching equilibrium after 96 h. All biochars and composites, regardless of feedstock type or pyrolysis temperature, exhibited lower K release rates compared to KCl. After 24 h (Table 5), KCl had released approximately 88% of its total K content, consistent with previous studies [35,36], indicating that K from charred matrices is released more gradually than K from KCl. Therefore, applying high rates of K-rich biochars to soil should be managed carefully to prevent excessive K accumulation in the soil solution and potential K leaching.

Table 5. Potassium (% of total K) released in CaCl₂ solution over 24 and 672 h for all treatments.

Treatment	K Released in 24 h (% Total K)	K Released in 672 h (% Total K)
BBP300	35.7 h	42.0 f
BBP650	37.5 gh	42.8 f
BCH300	44.3 f	55.0 bc
BCH650	39.8 g	46.5 e
BCM300	38.1 gh	52.8 cd
BCM650	38.7 g	45.6 e
CBP300	55.8 b	56.3 b
CBP650	50.6 de	51.7 d
CCH300	53.5 bc	55.7 bc
CCH650	50.3 e	56.9 b
CCM300	52.9 cd	56.5 b
CCM650	53.3 bc	54.3 bcd
KCl	88.0 a	88.1 a

The treatment means with the same letter do not differ via the Duncan test at $p < 0.05$. BBP: biochar banana peel; CBP: composite banana peel; BCH: biochar coffee husk; CCH: composite coffee husk; BCM: biochar chicken manure; CCM: composite chicken manure.

Among the pure biochars, BBP300 exhibited the lowest K release within the first 24 h, with 35.7% of its total K content released, whereas BCH300 released 44.3% over the same period. After 28 days, BBP300 remained the biochar with the lowest cumulative K release (42.0%), while BCH300 released the highest amount, reaching 55.0% of its total K. Among the composites, CCH650 had the lowest K release in the first 24 h (50.3% of total applied K), whereas CBP300 released the highest amount (55.8%). By the end of the 28-day period, CBP650 exhibited the lowest cumulative K release (51.7%), while CCH650 and CCM300 had the highest releases, each reaching approximately 57% of the total K being mixed with the washed sand. When comparing the pure biochars and composites, all the composites exhibited a higher K release within the first 24 h than their corresponding pure biochars, a result expected due to the presence of KCl mixed with the feedstocks during co-pyrolysis. However, by the end of the 28 days, CBP650 had the lowest cumulative K release among the composites (52%), which was 36% lower than that of KCl. Notably, CBP650 released K even more slowly than BCH300, which had a total release of 55%. These findings indicate that mixing KCl with a charred matrix is an effective strategy for slowing K release over time, potentially reducing K leaching in soils.

The pyrolysis temperature was a significant factor influencing K release from the pure CH and CM biochars. As the temperature increased from 300 °C to 650 °C, less K was released by the end of the 28-day incubation period. These results align with previous studies, which indicate that pyrolysis temperatures above 500 °C promote a more prevalent inorganic matrix and, surprisingly, result in fewer soluble K salts in biochars [9]. Conversely, BP biochars exhibited a similar K release at both 300 °C and 650 °C, with both amounts

being lower than those observed for the CH- and CM-derived biochars. This difference can be attributed to the specific characteristics of the BP-derived biochar, such as its higher cation exchange capacity (CEC) compared to the other BBFs. This property may influence how K is trapped, adsorbed, and released, as well as its overall availability, regardless of the pyrolysis temperature [87]. Therefore, in the BP biochars, the chemical structure and interactions with other components likely played a crucial role in controlling the rate of K release, leading to distinct behavior compared to the other biochars. Some of the biochars formulated in this study, regardless of pyrolysis temperature, are suitable for use as slow-release K sources while also reducing the proportion of KCl required in the final composite.

The lowest rates of K release in the first 24 h were observed for the BP biochars (Table 5). This can be attributed to their high ash content (Table 3) and highest cation exchange capacity (CEC) (Table 4) among the tested biochars, demonstrating that ash content can slow down K release from biochars [67]. Additionally, studies indicate that K release from organic fertilizers, such as biochar, differs from that of mineral fertilizers, which typically exhibit a release pattern proportional to their application rate. This difference arises from the complex interactions of K with organic and inorganic compounds [88]. Furthermore, the rate of K release depends on the concentration gradient between the biochar and the soil, as well as the equilibrium between the solid and liquid (solution) phases, highlighting the crucial role of time in the nutrient release process [67]. These results suggest that all biochars and composites exhibit a controlled release of K into the solution compared to soluble KCl. Supplying potassium to crops in combination with charred matrices can enhance K retention in the soil for a longer period, supporting plant uptake during critical growth stages when K demand is highest.

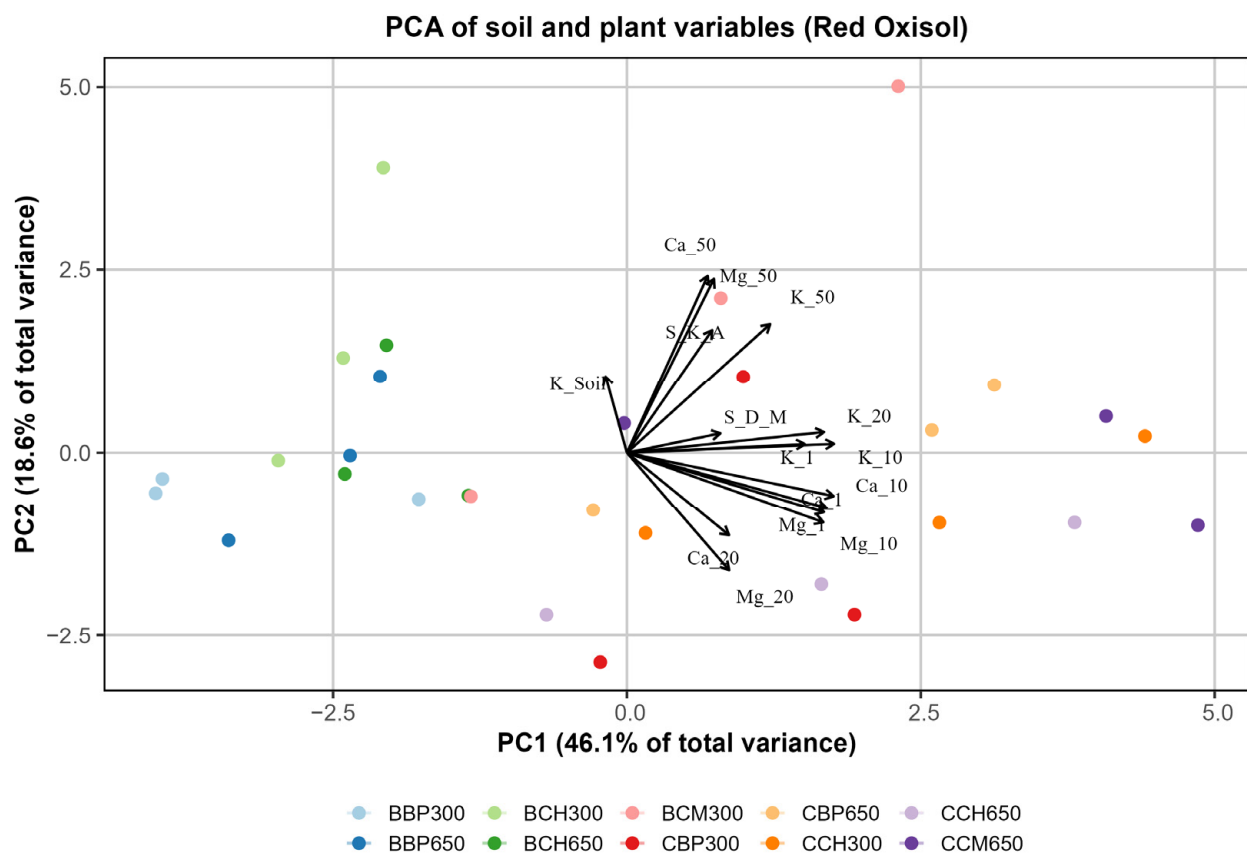
The accumulated K content at the end of 672 h (28 days) for all the pure and composite biochars was lower than that reported in other studies on organic K sources [28,37]. In a study evaluating the ability of bentonite co-pyrolyzed with *Canna indica* to enhance the K release capacity of BBFs, Chen et al. [28] found that co-pyrolysis reduced the total K released from 92.5% to 72.6% after 28 days. Similarly, Cheng et al. [37], who examined K release from composites prepared with distillers' grains, reported that their best composite released 82.35% of its total K in 24 days.

Potassium is highly susceptible to leaching through the soil profile, particularly in sandy soils [89]. Therefore, the development of fertilizers that promote slower K release can improve crop fertilization efficiency, reducing application costs, better meeting plant nutrient demands, and mitigating environmental issues associated with the high solubility and leaching of K from mineral fertilizers. According to ISO 18644 [90], controlled-release fertilizers should not release more than 15% of the nutrient within the first 24 h and no more than 75% over 28 days. In accordance with these guidelines, both pure biochars and composites meet the requirement of not exceeding 75% K release within 28 days, confirming their potential as slow-release fertilizers. However, none of the treatments comply with the first criterion, as they all release more than 15% of their K within the first 24 h. Similar results were observed by Fachini et al. [35], who evaluated BBFs produced by enriching sewage sludge with KCl. In their study, the powdered BBF also failed to meet the initial release criteria (K release within 24 h), necessitating physical modifications to the K fertilizers, such as the agglomeration of charred powder matrices into pellets or granules, to slow K release during the initial 24 h period.

3.3. Agronomic Effectiveness of Biochar–K Composites

Biochar can be used as a soil conditioner to enhance fertility and as a nutrient source for plants [29]. The K-BBFs formulated in this study demonstrated superior performance

in controlling K release compared to KCl. Consequently, an experiment was conducted with corn grown in two contrasting soils to evaluate the agronomic efficiency of K-BBFs in supplying K for optimal corn nutrition and growth. To assess the overall effects of different K-BBFs on corn growth in both soil types, Principal Component Analysis (PCA) was performed for each dataset (Figure 4). In Red Oxisol (RO) (Figure 4a), PC1 accounted for 46.09% of the variance, while PC2 explained 18.65%. In Red-Yellow Oxisol (RYO) (Figure 4b), PC1 accounted for 38.64% and PC2 for 20.41%. In both soils, a clear distinction was observed between the pure biochars and composite treatments, indicating significant differences in their effects on soil properties and nutrient availability. The primary factor driving cluster formation was the nutrient content in the soil solution, mainly the availability of K, Ca, and Mg. The addition of KCl during composite production influenced K release into the soil solution, resulting in distinct nutrient availability patterns and clusters. Additionally, PCA revealed that soil type plays a crucial role in K retention and mobility, affecting how treatments interact with soil chemistry. The differences in variance explained by PC1 and PC2 between RO and RYO soils suggest that nutrient dynamics and treatment responses are more structured in RO, whereas RYO exhibits a more dispersed pattern, indicating higher variability or additional influencing factors. These patterns guided further analysis, providing a deeper understanding of the effects of K-BBFs on soil properties and plant traits.



(a)

Figure 4. Cont.

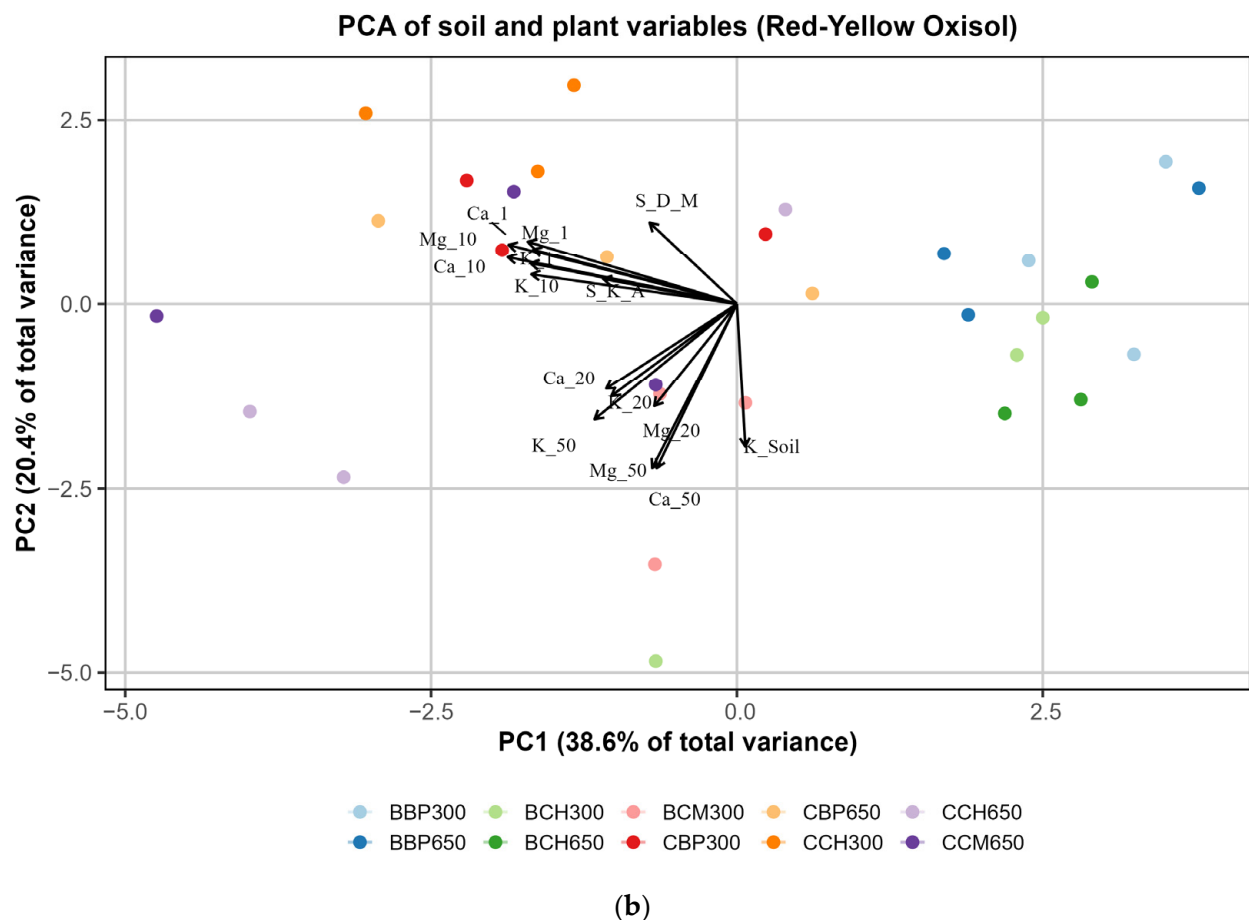


Figure 4. Principal Component Analysis (PCA) biplot illustrating grouping of treatments in RO (a) and RYO (b) based on soil and plant responses. S_D_M: shoot dry matter; S_K_A: shoot K accumulation; K_Soil: Residual K available in whole soil samples. Ca_1, K_1, Mg_1, Ca_10, K_10, Mg_10, Ca_20, K_20, Mg_20, Ca_50, K_50, Mg_50: Ca, K, and Mg concentrations in soil solution collected at 1, 10, 20, and 50 days after planting.

3.3.1. Dynamics of K Release from K-BBFs in Soil–Plant Systems

To understand the dynamics of K release from K-BBFs in the soil–plant system and how soil texture influences K availability for corn growth, soil solution from the pots was extracted at four different stages of corn growth: 1, 10, 20, and 50 days after planting (Figure 5). Even though the soil solution is not the main nutrient reservoir for plant growth, it reflects, when sampled in sequence, the controlled processes of the mineral and organic phases, ionic balance, solid–liquid soil phase equilibrium, and sorption/desorption reactions; thus, it reflects the processes that control the release rate of K into the soil solution. It also provides insight into the dynamics of K release from the solid phase to the soil solution for the applied fertilizers [91,92].

The release of nutrients from a fertilizer into the soil solution depends on both intrinsic factors, such as its nutrient content, the solubility of the K chemical species, and its physical form [93], as well as extrinsic factors, including soil water content and the soil's ability to retain nutrients in soil colloids. This retention capacity is directly influenced by the mineralogical composition of the soil, particularly its clay content and cation exchange capacity (CEC) [36,94]. The K levels released into the soil solution varied significantly between the two soils (Figure 5), demonstrating that soil texture was the primary factor regulating K availability in this study. The K concentrations in solution were significantly higher in the Red-Yellow Oxisol (RYO) than in the Red Oxisol (RO). In the first extraction for the CCH300 treatment, the K levels in the RYO exceeded 1100 mg L^{-1} , whereas the

same treatment in the RO yielded less than 410 mg L^{-1} . This difference can be attributed to variations in clay and organic matter content, as well as CEC, between the two soils. The RO contained 620 g kg^{-1} of clay, whereas the RYO had 470 g kg^{-1} . The treatment with the lowest K levels was BBP300, with 123 mg L^{-1} in the first extraction for the RO and 434 mg L^{-1} for the RYO. This further highlights the significant role of feedstock type in regulating the release of K from biochar into the soil solution, as previously observed in the kinetics experiment. Given the high levels of K in solution, K application through biochar in sandy Oxisol should be performed in split applications. To optimize nutrient availability, biochar or its composite should be applied both at planting and as a topdressing.

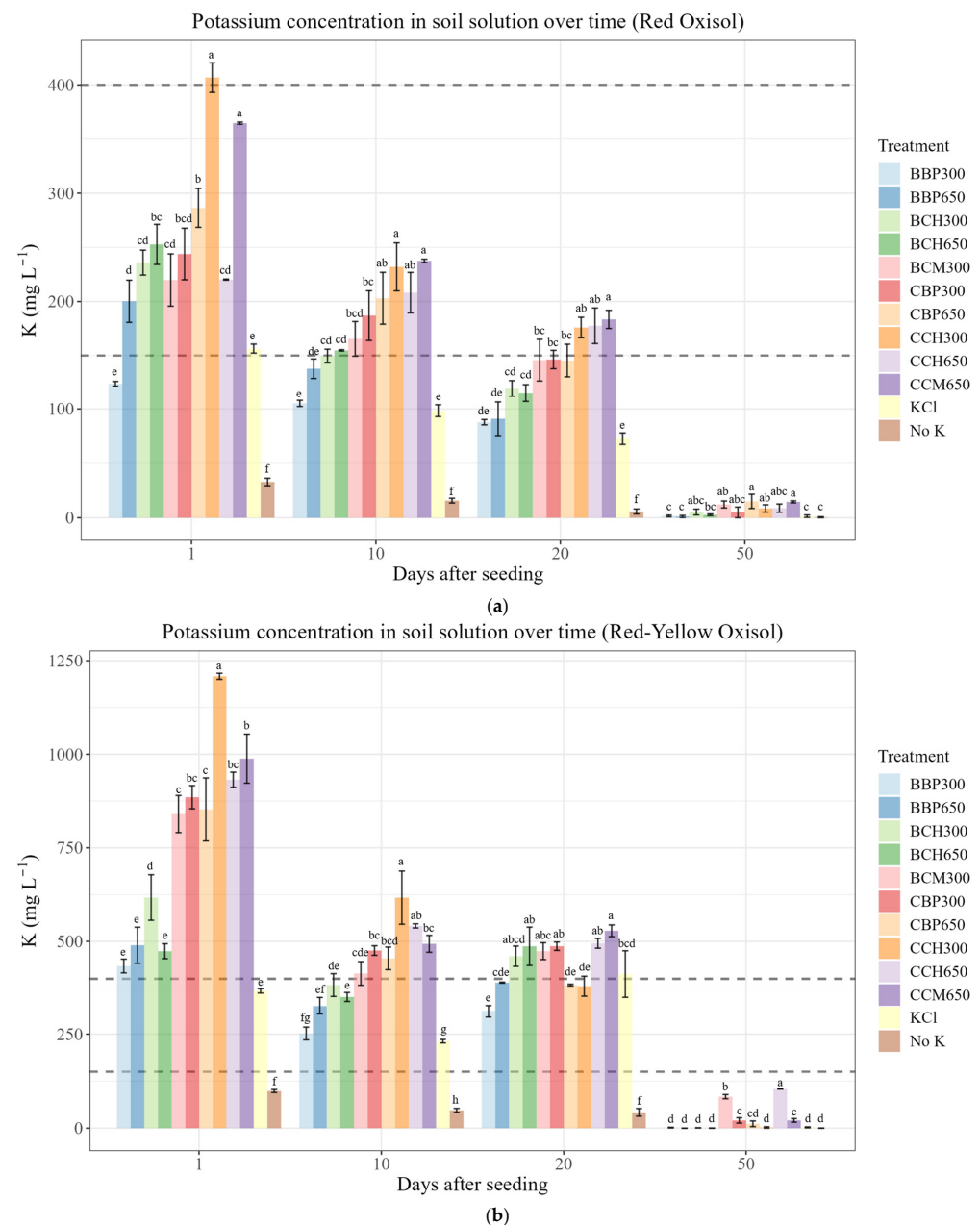


Figure 5. K contents analyzed in soil solution collected at 1, 10, 20, and 50 days after planting. (a) Red soil. (b) Red-Yellow Soil. BBP: biochar banana peel; CBP: composite banana peel; BCH: biochar coffee husk; CCH: composite coffee husk; BCM: biochar chicken manure; CCM: composite chicken manure. Black dashed line represents ideal ($150\text{--}400 \text{ mg L}^{-1}$) range of K content in nutritive and hydroponic solutions [80,84]. Different lowercase letters indicate statistically significant differences among treatments for each sampling day, according to Duncan's test ($p < 0.05$).

The pyrolysis temperature also affected K release from the BBFs in both soils. This was clear in the first two extractions for RY, where the pure biochars produced at 650 °C released more K than those produced at 300 °C, especially for the rates of K release verified for the BP and CH biochars and their composites. In the RYO, the trend was similar for the BP biochars but different for the CH biochars. By the third extraction, 20 days after seeding, differences in K release between the pyrolysis temperatures were still observed, though without a clear pattern. For the composites, K release was significantly higher than the pure biochars in the first, second, and third extractions for both soils. This increase was expected due to the addition of KCl in the co-pyrolysis and composite synthesis, as also demonstrated by the kinetic study performed in lysimeters. According to Hoagland and Arnon [95], the ideal K concentration in a nutrient solution for soil-less plant cultivation is 234 mg L⁻¹, but this concentration may fluctuate over time, as the nutrient demand of the plant varies according to its growth stage. This value considers the nutrient balance, pH, and EC of the solution and can serve as a threshold limit for ideal nutrient levels released into the soil solution by different fertilizers. However, the ideal potassium concentration in the nutrient solution can depend on various factors, such as the plant species, the concentration of other nutrients, and the type of system used, with this concentration ranging from 150 to 400 mg L⁻¹ [96–100]. For the RYO, all treatments, including the pure biochars, exceeded the upper limit of the suitable range in the first extractions. In contrast, for the RO, only the CCH300 treatment surpassed this value in the first extraction. This indicates that, although the BBFs exhibited a slower release dynamic compared to KCl in the kinetics test, it is evident that in a more complex system, such as the soil–plant system, external factors such as soil texture, CEC, fertilizer CEC, soil OM level, etc., play a crucial role in regulating the K release dynamics from BBFs.

In this study, the application of KCl (positive control) was divided into four doses. As a result, the K concentration in the soil solution of the KCl treatment cannot be directly compared to that of the other treatments. However, it was observed that, in the RYO, the K concentrations in the KCl treatment were much higher than in the RO, approaching the upper limit of 400 mg L⁻¹. This suggests that, even when applied in split doses, K supplied through KCl remains at high concentrations in the soil solution in soils with lower clay contents. This could lead to K leaching through the soil profile in field conditions, resulting in nutrient losses and negatively affecting crop growth and yield. Since K content in the soil solution can fluctuate depending on soil type, this range may include specific cases, such as the RYO. The potassium levels in the solution of the sandy Oxisol are excessively high. Therefore, even when supplied in combination with biochar, K from composites should be applied in split doses to enhance K use efficiency in soils where sand predominates over clay, particularly in soils with low CEC. In addition to the high solubility of KCl, which necessitates its application in multiple doses, its high chloride content can be harmful to certain crops [5,8,101,102]. Consequently, the higher the K content in a feedstock, the greater the likelihood of producing a biochar that is both K-rich and low in chloride, providing an effective K supply while reducing the need for KCl and excess Cl⁻ in composite formulations. If not correctly managed, the risk of chloride—a micronutrient—toxicity in soils worldwide may be a serious concern for some crop production, given that KCl is the primary source of K used in agriculture.

It is essential to understand the influence of K in the soil solution on plant growth and the pattern of K uptake by plants. To evaluate the ability of each selected treatment to supply K for corn growth in contrasting soils, a greenhouse pot experiment was conducted over 50 days. Observing the K levels in the soil solution, it is evident that K concentrations decreased over time in all the treatments across both soils, indicating its uptake by corn plants. According to Gamboa [103], the rate of K uptake is relatively slow during the first

30 days after germination but then increases significantly, maintaining a steady growth rate for an additional 20 to 25 days. This explains the sharp decline in K levels in the solution between the third and fourth extractions. In the RYO, K levels fell below 105 mg L^{-1} in the fourth extraction, whereas in the RO, they dropped below 16 mg L^{-1} during the same period. The dynamics of Ca and Mg release were also evaluated on the same days as K (Figures A1 and A2, Appendix A). Similarly to K, Ca and Mg concentrations in the RYO solution were generally higher than in the RO, indicating that soil texture also influences their behavior. Additionally, the strong correlation between Ca and Mg (Figure A3, Appendix A) suggests that these elements exhibit similar dynamics in the soil solution, likely due to their bivalent nature and their combined supply through liming. In contrast, K, being monovalent, follows a different pattern and may be more susceptible to leaching in soils.

3.3.2. Effect of K-BBFs on Corn Growth and Nutrient Uptake

At the end of the experiment, shoot dry matter production was evaluated (Figure 6a,b). All the treatments significantly differed from the negative control in both the RO and RYO, indicating the composites' agronomic efficiency in supplying K to corn plants. In the RO, the treatments showed no differences among themselves and were as effective as KCl in nourishing corn plants. In the RYO, some variations were observed: CBP300 and CBP650 yielded the highest biomass production, comparable to KCl, whereas BCH300 and BCH650 resulted in lower production compared to other treatments, excluding the pots with no K supply. These differences may be related to the differences in the physicochemical properties of the biochars and their distinct interactions within the fertilizer–soil–plant system. Similar trends have been observed in other studies using biochar-based amendments. For instance, Yang et al. (2024) [104] reported that biochar application improved plant nutrient uptake and biomass production, with significant increases in potassium accumulation depending on the biochar characteristics. Elsaman et al. (2025) [105] also demonstrated that biochar-enriched fertilizers enhanced shoot biomass and K uptake in corn plants, emphasizing the role of K-rich biochars in improving nutrient availability and promoting crop growth under tropical conditions.

Regarding K accumulation in corn plants (Figure 6c,d), differences can be observed among treatments for both soil types. In both soils, all treatments showed significantly higher K accumulation than the control without any K source supply to corn plants, indicating that, in addition to supporting effective biomass production, the K provided by the BBFs was efficiently taken up by the corn plants. The highest K accumulation was seen in the KCl control for both the RO and RYO soils. For the RO, the treatments BCH300, BCM300, and CCM650 were statistically similar to KCl, while in the RYO, none of the treatments achieved K accumulation comparable to KCl. These results align with those of Yang et al. (2024) [104], who also noted that the agronomic performance of biochar-based fertilizers may vary with soil type and biochar source, affecting nutrient retention and plant uptake. Considering that biomass production was similar but the K accumulation in the treatments was slightly lower, it can be inferred that the higher K uptake in the positive (KCl) control treatment represents a form of luxury consumption, in which increased K uptake does not result in higher biomass production [106].

These results demonstrate practical implications in agriculture aimed at optimizing K supply in different types of soil. The biochars and composites produced in this work, mainly those derived from BP, offer a sustainable alternative to mineral fertilizers, such as KCl, promoting a gradual release of the nutrient that aligns with the plant's demand during its growth. However, it is important to know the fertilizer–soil–plant interface well

so that applications can be adapted to maximize nutrient use efficiency and crop yield, while avoiding soil K leaching.

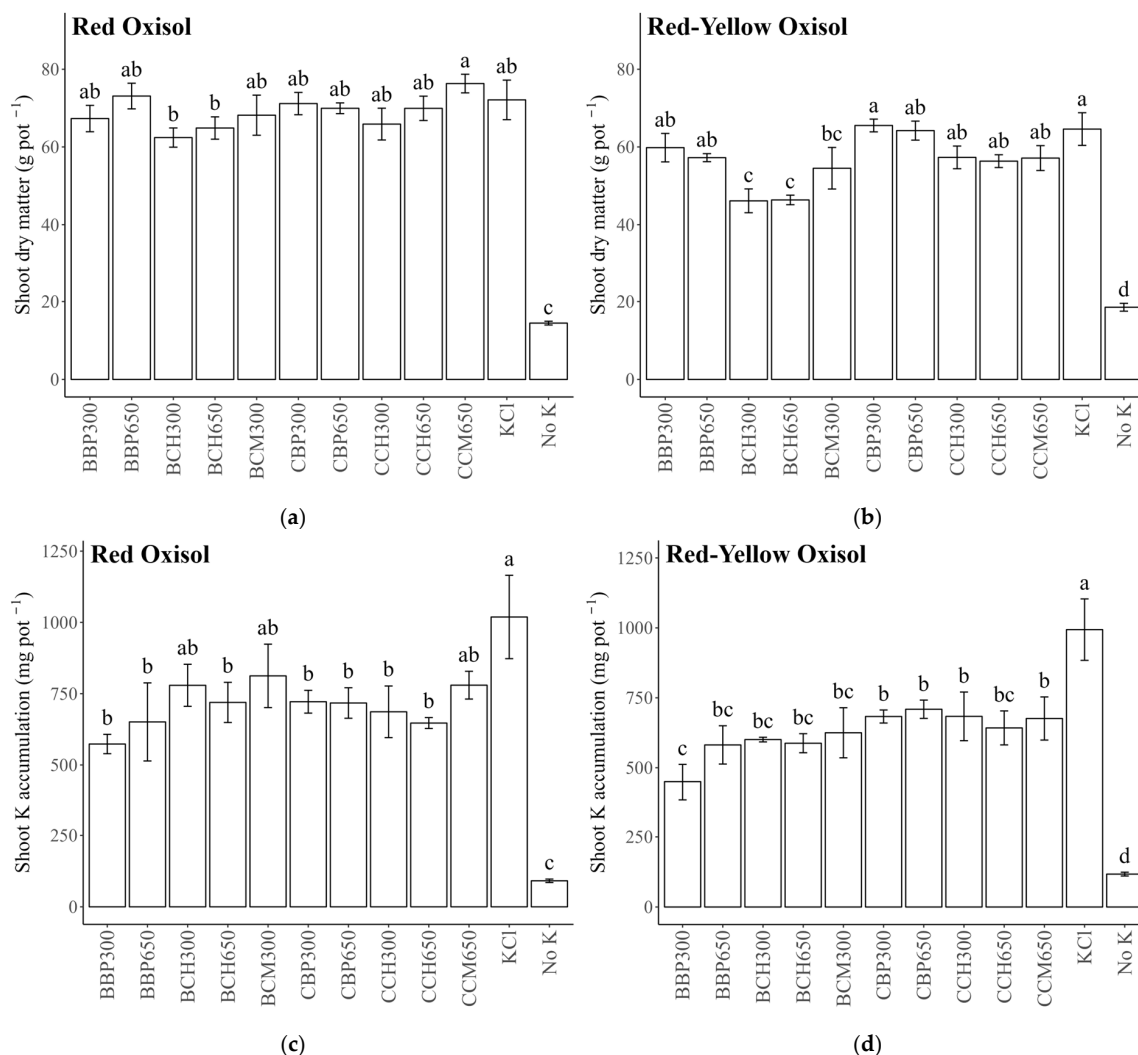


Figure 6. The shoot dry matter production (a,b) and potassium (K) accumulated in corn shoots (c,d) for plants cultivated in the Red and Red-Yellow Oxisols for all the treatments, compared to the positive control (KCl) and negative control (without K addition). The treatment means with the same letter do not differ by Duncan's test at $p < 0.05$. BBP: biochar banana peel; CBP: composite banana peel; BCH: biochar coffee husk; CCH: composite coffee husk; BCM: biochar chicken manure; CCM: composite chicken manure.

3.3.3. Residual Soil Potassium After Corn Harvest

It is possible to observe that the residual K content in the soil after corn cultivation (Figure 7) was lower for the BBFs compared to KCl for all the treatments in both the RO and RYO. This behavior can be explained by the K chemical species present in the K-BBFs. As demonstrated in the release kinetics experiment (Figure 3), the K-BBFs exhibit a much slower release of K than KCl, indicating a likely greater retention of K in the BBFs in less soluble forms and, therefore, K being less readily available to the soil compared to in KCl. This characteristic of the BBFs contributes to their gradual release of K, which can be beneficial in agricultural systems that require a slower and more continuous availability of K throughout crop growth stages, as observed in corn cultivation. Moreover, since the stability of biochar in the soil environment is variable, being highly dependent on the characteristics of the biochar and the soil–plant system in which it is applied, it is known that the physicochemical and biological properties of biochar can change significantly

over time as the material ages [9]. Therefore, studies evaluating biochar aging in complex fertilizer–soil–plant systems are also necessary to understand its fate and the effects of aging on potassium availability for crops grown in succession.

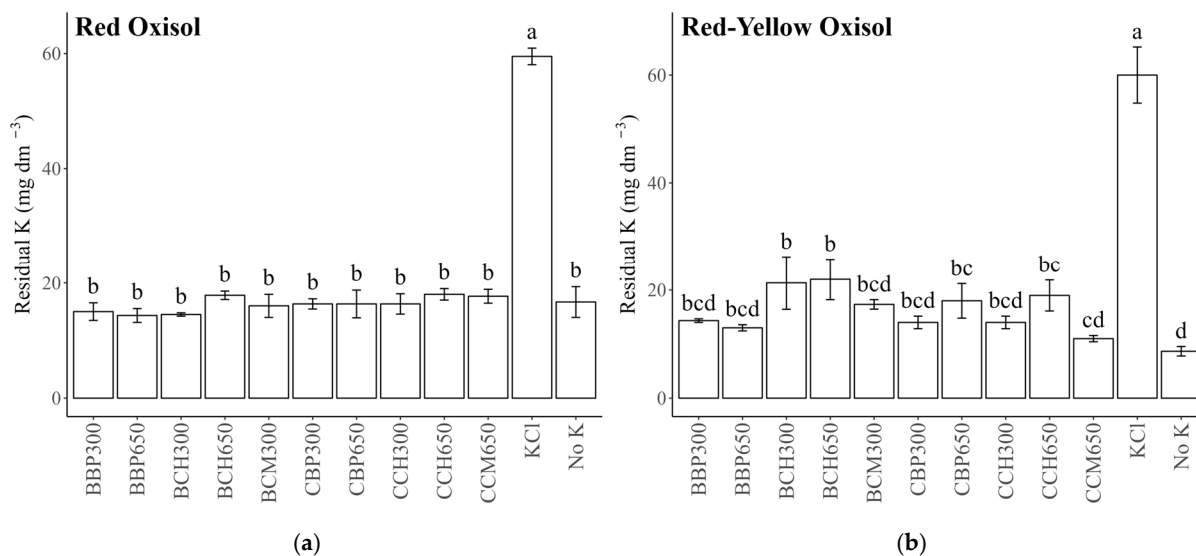


Figure 7. Residual K available in whole soil samples of Red (a) and Red-Yellow (b) Oxisols after 50 days of corn cultivation for all treatments, compared to positive control (KCl) and negative control (without K addition). Treatment means with same letters do not differ by Duncan's test at $p < 0.05$. BBP: biochar banana peel; CBP: composite banana peel; BCH: biochar coffee husk; CCH: composite coffee husk; BCM: biochar chicken manure; CCM: composite chicken manure.

4. Conclusions

The use of potassium-rich biochars offers a viable and sustainable alternative to conventional KCl fertilization, particularly in tropical regions such as Brazil, which has highly weathered and potassium-deficient soils. Among the feedstocks tested, banana peel proved to be the most promising raw material for the production of biochar-based potassium fertilizers (K-BBFs), showing the potential to replace up to 82% of KCl (CBP650) or even replace it completely (BBP300 and BBP650) in corn cultivation. Its high K content, slower release rate, and agronomic effectiveness support its adoption, especially in systems aiming to reduce dependence on KCl. For practical application, farmers cultivating in sandy Oxisols should consider split applications of powdered K-BBFs to reduce nutrient leaching, avoid imbalances of K, Ca, and Mg in the soil solution, and improve potassium use efficiency. In these soils, the rapid release of K can compromise crop nutrition due to cation competition. Additionally, pelletizing K-BBFs may enhance K retention and help meet international standards for slow-release fertilizers, improving their suitability for field application. While biochars derived from coffee husk and chicken manure also showed promise, further studies are needed to optimize their formulations. Lastly, field trials are essential to evaluate long-term K availability, leaching potential, and crop performance under field conditions. This approach strengthens the foundation for recommending K-BBFs as an effective and regionally adaptable strategy for potassium fertilization in Brazilian agriculture.

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Appendix A

Appendix A.1

Table A1. K release kinetic coefficients in CaCl₂ solution for BBFs and KCl.

Treatment	Linear			Exponential			Power Function			Elovich			Toth			Gompertz		
	R ²	RMSE	AIC	R ²	RMSE	AIC	R ²	RMSE	AIC	R ²	RMSE	AIC	R ²	RMSE	AIC	R ²	RMSE	AIC
BBP300	0.55	4.40	180.04	0.53	4.51	181.58	0.86	0.08	−59.89	0.53	4.51	181.58	0.88	2.30	143.18	0.90	2.07	136.84
BBP650	0.46	5.30	191.18	0.44	5.39	192.25	0.75	0.12	−37.04	0.44	5.39	192.25	0.79	3.34	165.52	0.81	3.17	162.27
CBP300	0.13	2.66	149.90	0.13	2.66	149.94	0.91	0.02	−154.05	0.13	2.66	149.94	0.95	0.65	67.08	0.96	0.56	58.65
CBP650	0.19	3.86	172.25	0.18	3.87	172.35	0.87	0.04	−107.53	0.18	3.87	172.35	0.91	1.31	109.43	0.89	1.41	113.72
BCH300	0.53	7.57	212.59	0.50	7.78	214.27	0.93	0.09	−53.45	0.50	7.78	214.27	0.94	2.66	151.81	0.87	3.98	175.94
BCH650	0.61	3.27	162.26	0.60	3.33	163.39	0.91	0.04	−99.73	0.60	3.33	163.39	0.90	1.64	122.89	0.83	2.15	139.14
CCH300	0.10	6.02	198.85	0.10	6.03	198.9	0.72	0.08	−59.03	0.10	6.03	198.90	0.84	2.55	149.22	0.84	2.57	149.71
CCH650	0.29	8.97	222.79	0.27	9.04	223.27	0.95	0.07	−68.20	0.27	9.04	223.27	0.69	5.93	199.97	0.95	2.33	143.83
BCM300	0.52	10.05	229.60	0.49	10.46	232.00	0.90	0.23	3.55	0.48	10.46	232.00	0.94	3.56	169.29	0.85	5.58	196.25
BCM650	0.60	3.45	165.45	0.58	3.51	166.53	0.88	0.05	−84.38	0.58	3.51	166.53	0.87	1.94	132.99	0.82	2.32	143.70
CCM300	0.26	12.49	242.64	0.24	12.61	243.21	0.93	0.16	−19.29	0.24	12.61	243.21	0.96	2.85	155.89	0.96	2.92	157.43
CCM650	0.18	2.24	139.50	0.18	2.24	139.54	0.94	0.01	−171.48	0.18	2.24	139.54	0.98	0.34	28.88	0.96	0.50	51.64
KCl	0.06	1.84	127.72	0.06	1.84	127.72	0.81	0.01	−187.18	0.06	1.84	127.72	0.96	0.40	37.48	0.96	0.39	36.94

Appendix A.2

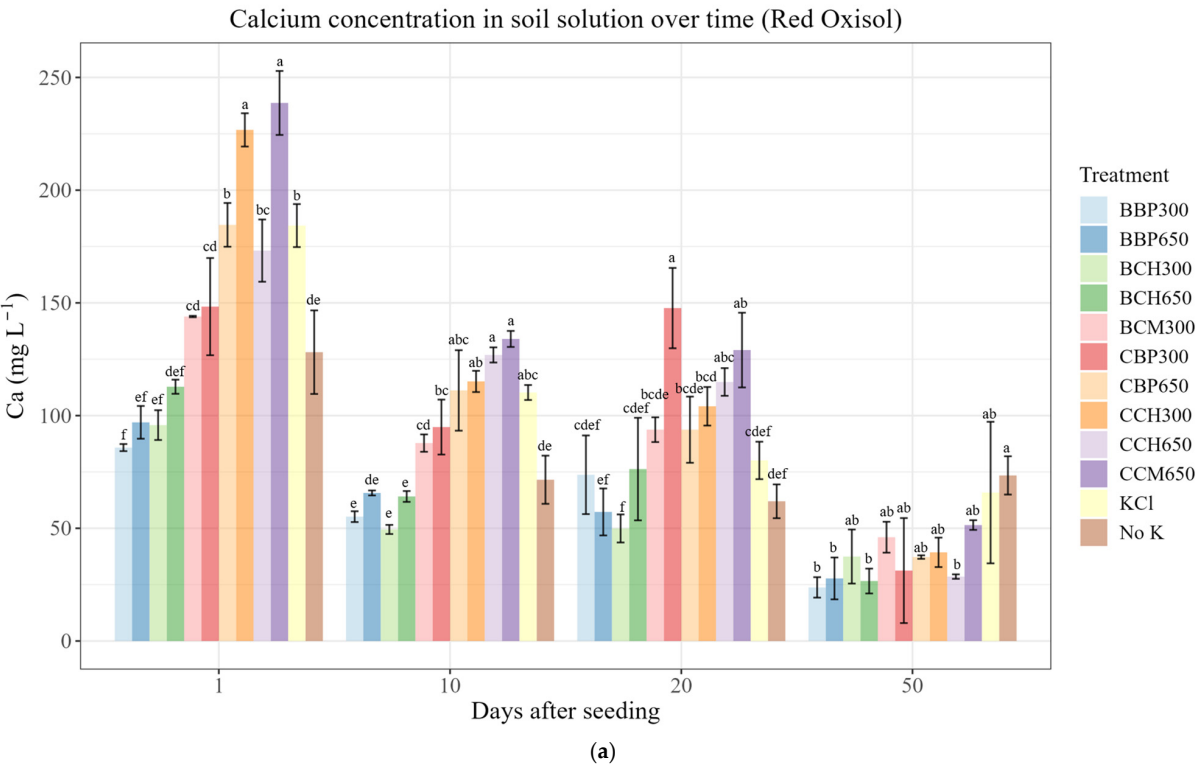


Figure A1. Cont.

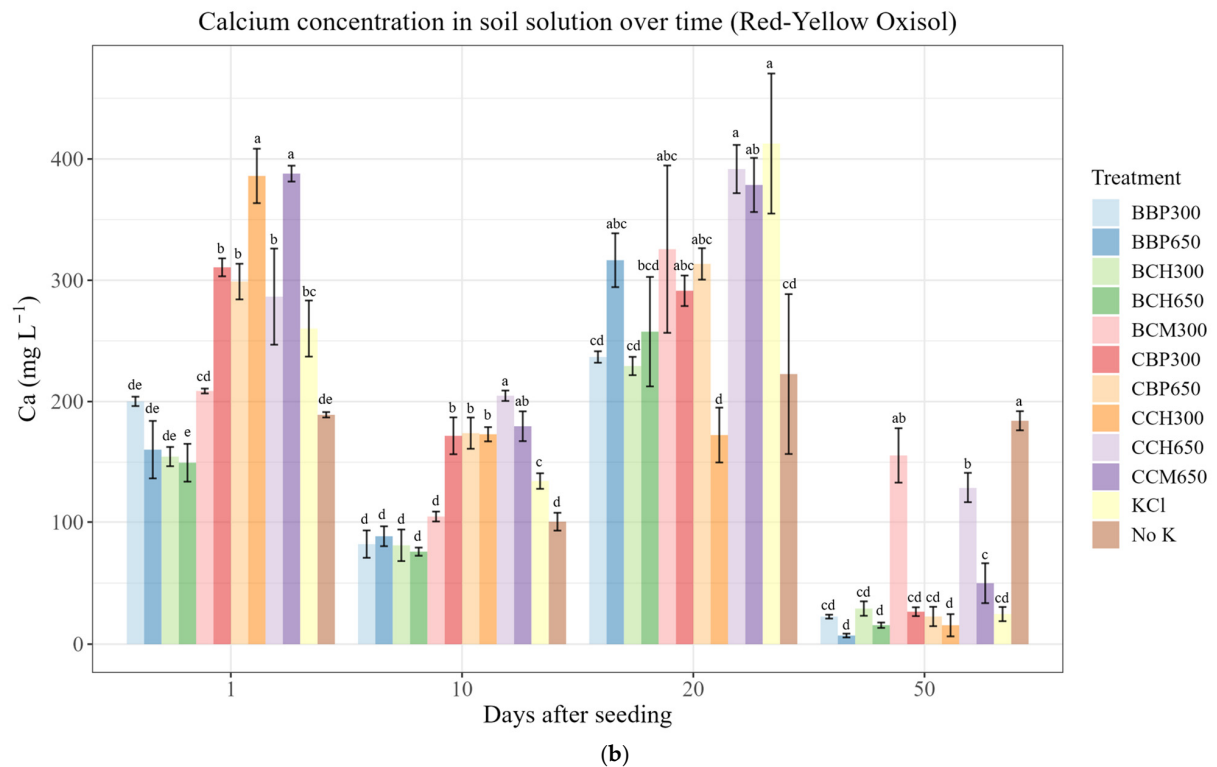


Figure A1. Ca contents analyzed in soil solution collected at 1, 10, 20, and 50 days after planting. (a) Red Oxisol. (b) Red-Yellow Oxisol. BBP: biochar banana peel; CBP: composite banana peel; BCH: biochar coffee husk; CCH: composite coffee husk; BCM: biochar chicken manure; CCM: composite chicken manure. Different lowercase letters indicate statistically significant differences among treatments for each sampling day, according to Duncan's test ($p < 0.05$).

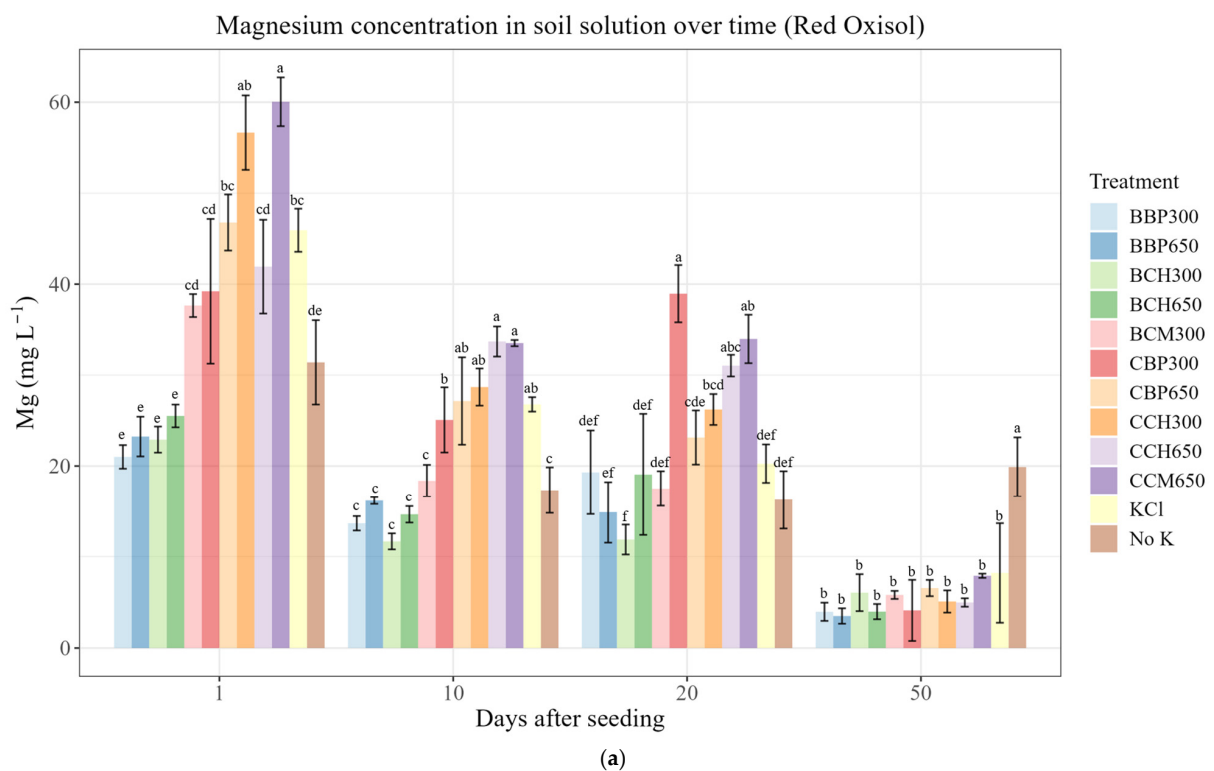


Figure A2. Cont.

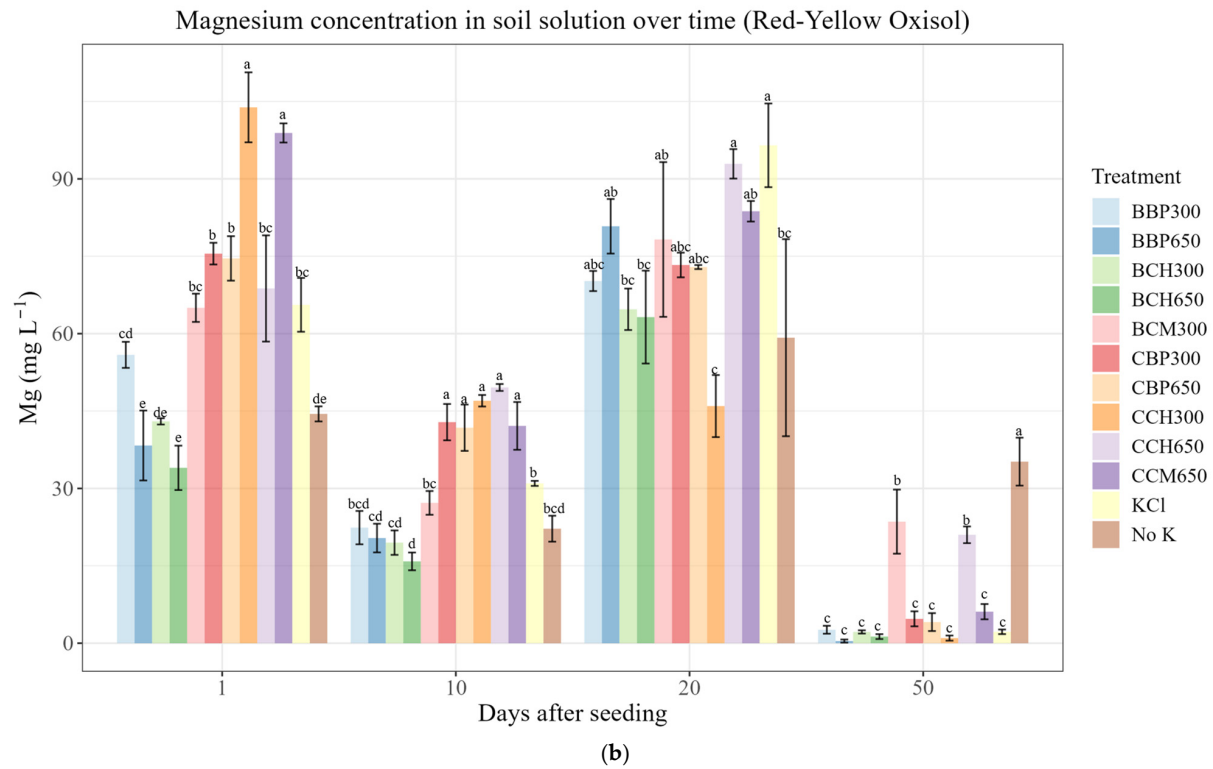


Figure A2. Mg contents analyzed in soil solution collected at 1, 10, 20, and 50 days after planting. (a) Red Oxisol. (b) Red-Yellow Oxisol. BBP: biochar banana peel; CBP: composite banana peel; BCH: biochar coffee husk; CCH: composite coffee husk; BCM: biochar chicken manure; CCM: composite chicken manure. Different lowercase letters indicate statistically significant differences among treatments for each sampling day, according to Duncan’s test ($p < 0.05$).

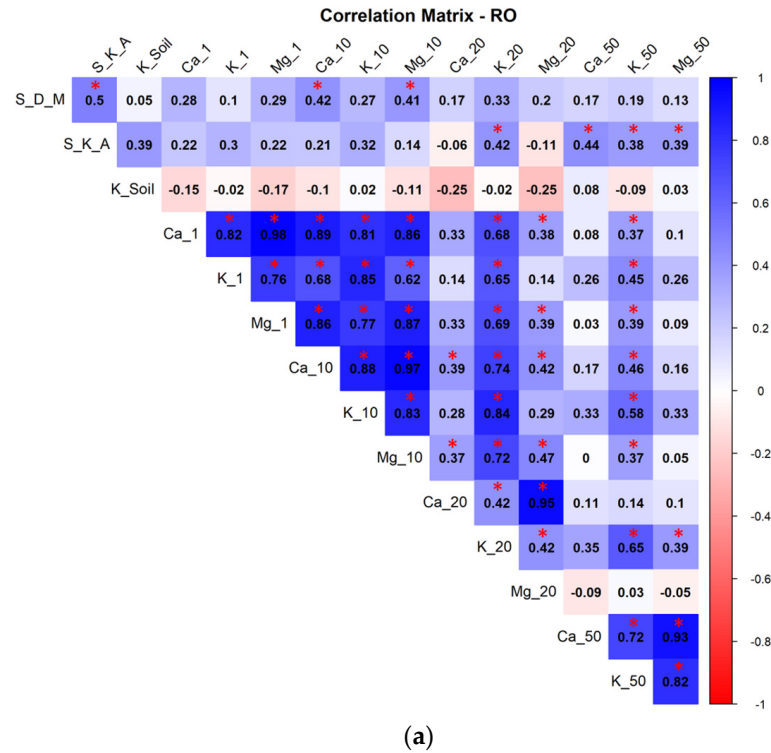


Figure A3. Cont.

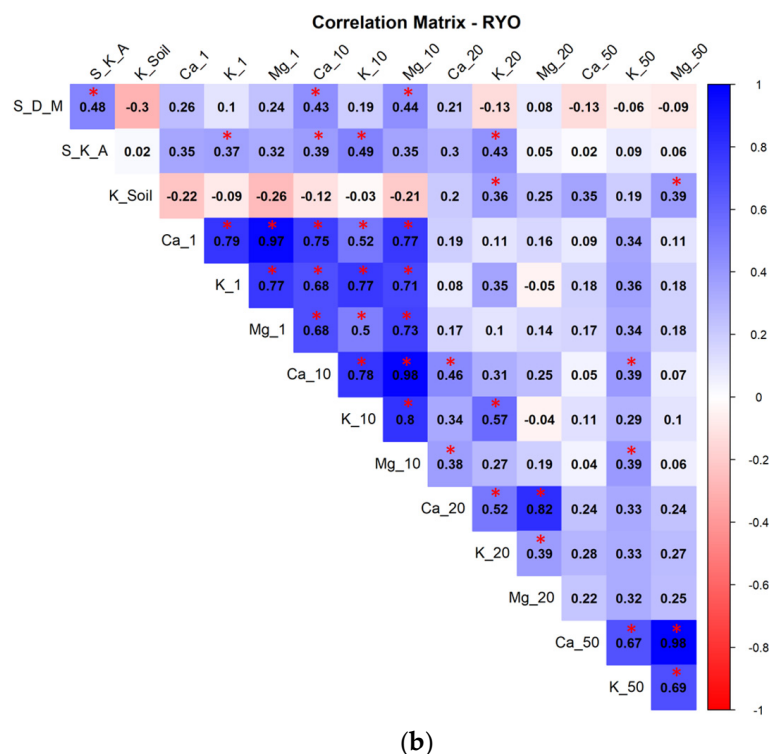


Figure A3. Pearson correlation matrix of soil chemical properties and corn growth in RO (a) and RYO (b). Red * indicates statistically significant correlations at $p < 0.05$. S_D_M: shoot dry matter; S_K_A: shoot K accumulation; K_Soil: Residual K available in whole soil samples. Ca_1, K_1, Mg_1, Ca_10, K_10, Mg_10, Ca_20, K_20, Mg_20, Ca_50, K_50, Mg_50: Ca, K and Mg concentrations in soil solution collected at 1, 10, 20, and 50 days after planting.

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