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Enhancing Cation Exchange Capacity of Weathered Soils Using Biochar: Feedstock, Pyrolysis Conditions and Addition Rate

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Abstract: The addition of alkaline and high-cation exchange capacity (CEC) biochars is a suitable strategy to increase the CEC of weathered soils. The aim of this study was to evaluate the effect of biochar from different feedstocks and pyrolysis temperatures on the CEC of two contrasting Oxisols. Biochars produced from chicken manure (CM), eucalyptus sawdust (ES), coffee husk (CH) and sugarcane bagasse (SB),plus a control (without biochar), at 350, 450, and 750 °C were mixed with the soils at 2; 5; 10 and 20% (*w*/*w*) and incubated for 9 months. Feedstock, pyrolysis temperature and addition rate of biochar were key factors controlling the alteration of soil CEC. The CH biochar pyrolyzed at 350 °C was the most effective matrix at increasing soil CEC. In a rate-dependent way, ES and SB biochars increased C contents of both soils without improving soil CEC. The efficiency of high-ash biochars in enhancing soil CEC in both Oxisols was limited by the alkalization caused by high rates of CH and CM biochars. The increase in CEC is soil-dependent and modulated by high-ash biochar CEC and application rate, as well as by the original soil CEC.

Keywords: thermal stability; aging; high-ash biochar; biochar aromatic character; chicken manure; coffee husk; biochar agronomic rate

1. Introduction

Brazilian weathered soils are characterized by high levels of Al^{3+}, low availability of nutrients (mainly P) and a clay fraction dominated by low chemical activity minerals, resulting in extremely low cation exchange capacity (CEC) [1]. Under native "cerrado" vegetation, the median value for CEC of typical Brazilian soils is 1.1 $cmol_c$ dm^{-3}, and 96.5% of the samples present a CEC< 4 $cmol_c$ dm^{-3} [2]. In such conditions, most of the negative charges are developed on the surface of organic matter colloids, which explains the strong correlation between CEC and organic C in these soils [3]. Increasing CEC in weathered soils by adding exogenous sources of C such as those contained in crop residues or other organic wastes is not a simple task, since the decomposition of the added C is favored by the large

soil microbial activity in warm and moist conditions of humid tropical areas, compared to temperate regions [4]. Crop residues represent 80% of biomass produced worldwide (8201 Tg y^{-1}) of which 38%, after pyrolysis, are eligible to act as nutrient sources to plants and inputs to improve fertility and C content of weathered tropical soils [5,6].

The use of biochar as a soil amendment has attracted increasing attention [7,8]. The motivation for producing biochar was stimulated by the high fertility status and high CEC of the Terra Preta de Índio (TPI) (Amazonian Black Earth) soils found scattered within a landscape predominantly of highly weathered and acidic tropical soils known as Latosols and Argissols (Oxisols and Ultisols by USDA Soil Taxonomy). Aromatic black C found in TPIs assures a high persistence of C compounds in soils of these regions [9–11]. Anthropogenic fertile soils have stimulated scientific investigation to converting organic wastes into biochar, since black C was hypothesized to be the primary reason for the high soil organic matter (OM) content, improved nutrient availability, and high CEC [12–14]. The efforts to use biochar in soil as a black C amendment can recreate artificial black earths in a short period, with the potential to overcome the limitations of Brazilian soils to grow crops such as high acidity, low reservoirs of available nutrients and reduced CEC.

Although biochar is principally recalcitrant in nature and is decomposed at a slower rate than fresh residues, it also contains organic functional groups that could increase soil CEC and, consequently, adsorption of nutrients and heavy metals [15–18]. The negative charge density on biochar surface is increased because pyrolysis introduces polar organic moieties such as carboxylic acids, ketones and aldehydes due to depolymerization of cellulose and lignin [17,19–21]. Therefore, biochar CEC will depend on the feedstock and pyrolysis temperature [22–26]. High-ash feedstocks are potential sources to produce biochar with greater CEC than wood and other low-ash wastes. During pyrolysis, elements such as Mg, K, Na, and P can catalyze the formation of surface oxygen groups, such as carboxylic acids, lactones, and phenols, which increase the negative charge density of biochars [27–29]. As pyrolysis temperature increases, the loss of O and H on the biochar surface results in a drastic reduction in the biochar CEC [30–32]. For instance, the abundance of carboxylic and phenolic groups decreases at high temperatures, which is the reason why CEC is inversely correlated with pyrolysis temperature [33]. The high presence of aromatic moieties and graphitized ordered structures and low amounts of polar organic functional groups explain the lower CEC and decreased susceptibility to oxidation of charred matrices produced at higher pyrolysis temperatures (> 600 °C) [27,34]. In addition to pyrolysis temperature, the development of negative charges on biochar surface is pH-dependent, which is analogous to humic substances [30,35]. Thus, the effect of biochar on soil CEC is due not only to the original CEC of biochar, but also to the application rate and liming value of biochar added to soil, in line with Domingues [28]. According to Jieng and Wang [36], the incubation for 105 days of a Leucaena wood waste-derived biochar at 2.5%, and 5% (*w*/*w*) rates significantly increased the pH of a weathered soil from 3.9 to 5.1, CEC from 7.41 to 10.8 $cmol_c$ kg^{-1}, base saturation from 6.4 to 26%, microbial biomass C, as well as reduced soil erosion over the control (unamended).

Although several studies report positive contribution of biochar to soil CEC [37–39], the mechanism behind soil CEC increase in short and medium-term experiments is not clear [40,41]. In that direction, the evaluation of CEC of soils amended with biochar should be supported by other studies based on the use of tailored biochars from feedstocks exposed to variable temperatures and added to soils with varying OM and clay contents. We hypothesized that the application rate, pyrolysis temperature and ash content of biochars are the main factors driving its impact on soil CEC. It is also hypothesized that high-ash biochars prepared at relative low temperatures (≤ 450 °C) would be more effective than wood-derived biochars to increase soil CEC. The aim of this study was to investigate the effect of addition rates of contrasting feedstock and pyrolysis temperature-derived biochars on the enhancement of CEC of two weathered soils of different texture and OM content in a short-term incubation study.

2. Materials and Methods

2.1. Biochar and Soil Characterization

Biochar samples were produced from chicken manure (CM), eucalyptus sawdust (ES) (*Eucalyptus* ssp.), coffee husk (CH) (*Coffea* ssp.) and sugarcane (*Saccharum* ssp.) bagasse (SB). The feedstocks were chosen based on their availability in Brazil and due to their contrasting composition in terms of alkali metals, mainly K, and classes of organic components (cellulose, hemicellulose, and lignin) [28], which were expected to generate contrasting CEC values of the produced biochars.

The slow pyrolysis procedure was carried out in a muffle furnace with automatic temperature control and condensers for cooling the condensable gases that make up the pyroligneous acid. The feedstocks were oven-dried at 105 °C until constant weight and then heated up to the desired temperature (350, 450 and 750 °C), at constant heating rate of 1.67 °C/min and kept for 30 min at the final temperature. For convenience, biochars were referred to by the feedstock abbreviation followed by the pyrolysis temperature. For instance, CH350 stands for coffee husk pyrolyzed at 350 °C. The pyrolysis temperatures were chosen based on the degradability of precursor components from feedstocks and stability of the biochars formed [21]. Thus, 350 °C was selected to create biochar with functional groups capable to generate negative charges; 450 °C was chosen as an intermediate temperature that completely degrades hemicellulose and cellulose and still preserves some organic functional groups. In contrast, 750 °C stabilizes C through aromatization and strongly reduces the functional groups that bolster CEC. With these assumptions, the contrasting effects of the pyrolysis temperature on CEC could be evaluated.

Selected chemical and physicochemical properties of the biochars are shown in Table 1. The volatile matter and ash concentrations were determined according to standard procedure D-1762-84, established by the American Society for Testing and Materials [42]. The total C was determined by dry combustion using a total carbon analyzer (Vario TOC cube, Elementar, Germany). Biochar pH was determined in deionized water at a 1:10 (*w*/*v*) ratio. The biochar CEC was determined by the modified ammonium acetate compulsory displacement method, adapted to biochar [28,43].

Table 1. Chemical and physicochemical properties of the dystrophic Red Latosol (RL) and Red-Yellow Latosol (RYL) soils.

Soil Property	Red Latosol [a]	Red-Yellow Latosol [a]
pH (1:2.5; H_2O)	4.3 ± 0.1	5.3 ± 0.1
H+Al ($cmol_c\ dm^{-3}$)	11.8 ± 0.1	2.9 ± 0.1
CEC [b] at pH 7 ($cmol_c\ dm^{-3}$)	16 ± 1.6	2.4 ± 0.5
Total C (%)	6.6 ± 0.4	2.5 ± 0.2
Exchangeable K ($mg\ dm^{-3}$)	51 ± 1.8	74 ± 1.2
Available P ($mg\ dm^{-3}$)	1.8 ± 0.1	0.7 ± 0.01
Ca^{2+} ($cmol_c\ dm^{-3}$)	0.6 ± 0.1	1.9 ± 0.1
Al^{3+} ($cmol_c\ dm^{-3}$)	1.9 ± 0.1	0.3 ± 0.05
Clay (%)	75 ± 0.9	23 ± 0.2

[a] According to the Brazilian Soil Classification System [44]. The standard error (±, n = 3) are presented after the mean of each attribute. [b] CEC—cation exchange capacity.

Two soils were chosen based on their contrasting properties, including clay and total C contents. Samples from the 0–20 cm soil layer were collected from a dystrophic Red Latosol and Red-Yellow Latosol [44] located in Lavras, Minas Gerais (MG), Brazil (21°14′ S, 45°00′ W) and Itumirim, MG, Brazil (21°19′ S, 44°52′ W), respectively. Both soils can be classified as Oxisols according to USDA Soil Taxonomy [45]. Soil samples were air-dried and sieved (<2 mm) prior to the incubation experiment. Soil properties are shown in Table 1, and determined according to analytical protocols described in Silva [46].

2.2. Laboratory Incubation and Experimental Design

Biochar samples (<0.25 mm) were homogenously mixed with each soil type (100 g) at five application rates: 0% (control), 2%, 5%, 10% and 20% (*w*/*w*). Samples were placed into 250 mL plastic containers with a lid with small holes (5 mm) to allow aeration. Three replicates of each treatment were prepared, placed randomly and incubated under laboratory conditions in a dark room at 25 °C for 9 months. The moisture was maintained constant at 70% of maximum soil water-holding capacity by regularly replacing water by weight differences during the incubation. A completely randomized experimental design was used including three pyrolysis temperature (350, 450, 750 °C) combined with four addition rates (2%, 5%, 10% and 20%, *w*/*w*) for each biochar (CM, ES, CH, SB) and soil type (Red Latosol and Red-Yellow Latosol). The incubation period was chosen based on a previous study (data not published) to allow enough time for the stabilization of the alkaline reactions among biochars and soils, even though longer-term experiments could be needed to allow for complete aging and functionalization of biochar [15].

2.3. Soil Analysis after Incubation

After 9 months of incubation, the soil samples were oven-dried at 65 °C and analyzed for pH, total C and CEC. The soil pH was determined in deionized water at the ratio of 1:2.5 (*w*/*v*), after shaking the slurry for 5 min, followed by 30 min of particle settling time. The total soil C was determined on a 0.2 g sub-sample of ground and sieved (<75 µm) by dry combustion using a combustion elemental analyzer (Vario TOC cube, Elementar, Germany). Soil CEC was determined by a modified ammonium acetate compulsory displacement method [28,43]. Briefly, 2.0 g of soil were leached with five portions of 20 mL deionized water to remove excess of salts with vacuum filtration and a 0.45 µm pore size filter. In sequence, samples were washed with a 1.0 mol L^{-1} sodium acetate (pH 8.2) three times, followed by five portions of 20 mL ethanol to remove free (not-adsorbed) Na^+ ions. Samples were then washed with 20 mL of 1.0 mol L^{-1} ammonium acetate four times to displace the Na^+ on the exchangeable sites of the soil. The leachates were collected and stored in a 100 mL volumetric flask, and Na^+ contents in leachates were determined by flame photometry. The CEC corresponds to the amount of Na^+ displaced per unit mass of soil or kg C in the biochar, expressed in $cmol_c$ kg^{-1}.

2.4. Statistical Analysis

The dataset was submitted to analysis of variance (ANOVA) for significant differences of the factors tested such as pyrolysis temperature, biochar rate and their interaction on the soil attributes investigated. When significant, the F-test was applied ($p < 0.05$) to discriminate the effect of pyrolysis temperature on the soil CEC. The linear regression was used to examine the effect of biochar rates on soil CEC. ANOVA was performed for each soil and biochar separately. The Pearson´s correlation analysis was performed to measure the association between CEC and other soil properties, such as C and delta pH (ΔpH). The ΔpH value hereafter is defined as the change in soil pH induced by biochar application compared to the control soil. Data were statistically analyzed using the SISVAR, a free software developed at the Federal University of Lavras [47]. To account for soil and biochar properties, a multiple linear regression model was performed to predict the final soil CEC. This was performed using the data analysis package in Microsoft Excel, following the model as described in Equation (1).

$$Predicted\ soil\ CEC = a + b\ CEC\ biochar\ weight + c\ CEC\ soil\ weight \quad (1)$$

In Equation (1), *CEC biochar weight* is the mass fraction of the biochar addition (e.g., 2% = 0.02), *CEC soil weight* represent the mass fraction of soil (e.g., 98% soil = 0.98), biochar CEC and soil CEC are the values for the CEC of the individual components, respectively, and final soil CEC is the final CEC of the mixture; *a*, *b* and *c* are the regression coefficients.

3. Results and Discussion

3.1. Biochar Properties

Some selected properties of biochar are shown in Table 2. A more detailed discussion of biochar properties used in this study is available in Domingues et al. [28]. Overall, the ash content was highly variable among the biochar samples, ranging from 0.7% to 56% and following the order of CM > CH > SB > ES. Volatile matter decreased and C content increased (except for CM) with increasing pyrolysis temperature. Biochar pH was in the alkaline range, except for the ES pyrolyzed at 350 °C. CEC of biochars was also highly variable ranging from 1.3 $cmol_c\ kg^{-1}$ (SB at 750 °C) to 72 $cmol_c\ kg^{-1}$ (CH at 450 °C). As the pyrolysis temperature increased the biochar CEC decreased, mainly for CH at 750 °C. The highest biochar CEC per kg C was observed for CM at 450 °C (151 $cmol_c\ kg^{-1}$), which may be attributed to the catalyst effect of the CM mineral fraction generating chemical functional groups [48]. Compared to other biochars, the ash protection effect was also evidenced in the CM biochar due to the high CEC value obtained at 750 °C (86 $cmol_c\ kg^{-1}$). High concentrations of alkali metals, mainly K, increase biochar yield and concentration of stable C, as well as the thermal stability of feedstock components during pyrolysis [48]. Silicon contents are variable among biochars and could play a role in protecting feedstock components against thermal degradation during pyrolysis, considering the C–Si coupling interaction effects on solubility and physicochemical properties, and higher C fixation of Si-derived charred matrices [49].

Table 2. Chemical and physicochemical properties of the biochars produced from four feedstocks pyrolyzed at 350, 450 and 750 °C.

Feedstock	T (°C)	Ash	VM	C	pH	CEC	
			%			$cmol_c\ kg^{-1}$	$cmol_c\ kg^{-1}$ C
Chicken Manure	350	52 ± 0.2	37 ± 0.3	31 ± 0.2	9.7 ± 0.01	41.6 ± 0.9	135 ± 3.0
	450	55 ± 0.2	31 ± 0.1	27 ± 0.5	10.2 ± 0.00	40.7 ± 0.9	151 ± 3.3
	750	56 ± 0.1	27 ± 0.1	25 ± 0.9	11.7 ± 0.02	21.3 ± 0.5	86 ± 2.0
Eucalyptus Sawdust	350	0.9 ± 0.0	37 ± 0.1	70 ± 0.3	5.9 ± 0.13	10.8 ± 0.2	5.6 ± 0.1
	450	0.7 ± 0.0	29 ± 0.1	79 ± 1.2	8.0 ± 0.02	2.2 ± 0.2	3.2 ± 0.3
	750	1.1 ± 0.0	6 ± 0.1	91 ± 2.0	9.3 ± 0.01	1.4 ± 0.3	1.8 ± 0.4
Coffee Husk	350	13 ± 0.1	35 ± 0.2	61 ± 1.0	9.7 ± 0.00	69.7 ± 1.3	115 ± 2.1
	450	13 ± 0.1	26 ± 0.3	61 ± 0.3	9.8 ± 0.00	72.0 ± 1.7	117 ± 2.8
	750	20 ± 0.0	18 ± 0.4	66 ± 1.3	9.8 ± 0.00	18.9 ± 0.6	29 ± 0.9
Sugarcane Bagasse	350	1.9 ± 0.0	35 ± 0.3	75 ± 0.6	7.0 ± 0.00	4.6 ± 0.3	12 ± 0.8
	450	2.1 ± 0.0	24 ± 0.3	82 ± 0.7	8.7 ± 0.01	1.8 ± 0.1	1.8 ± 0.1
	750	2.2 ± 0.0	8 ± 0.1	91 ± 1.0	9.7 ± 0.02	1.3 ± 0.3	1.1 ± 0.3

The standard error (±, n = 3) is presented after the mean of each attribute. Legend: T = pyrolysis temperature; VM = volatile matter; EC = electrical conductivity; CEC = cation exchange capacity. Source: data adapted from Domingues et al. [28].

3.2. Soil Cation Exchange Capacity

The CEC values measured in the amended soils after 9 months of incubation were affected by biochar addition rates. Increasing the application rate of CM and CH biochars augmented the CEC of both soils (Figure 1A,C,E,G). On the other hand, the addition of ES (Figure 1B,F) and SB (Figure 1D,H) biochars did not increase the soil CEC. In fact, a statistically significant reduction in CEC was observed for some of the soil–biochar combinations (Figure 1B,D,F,H).

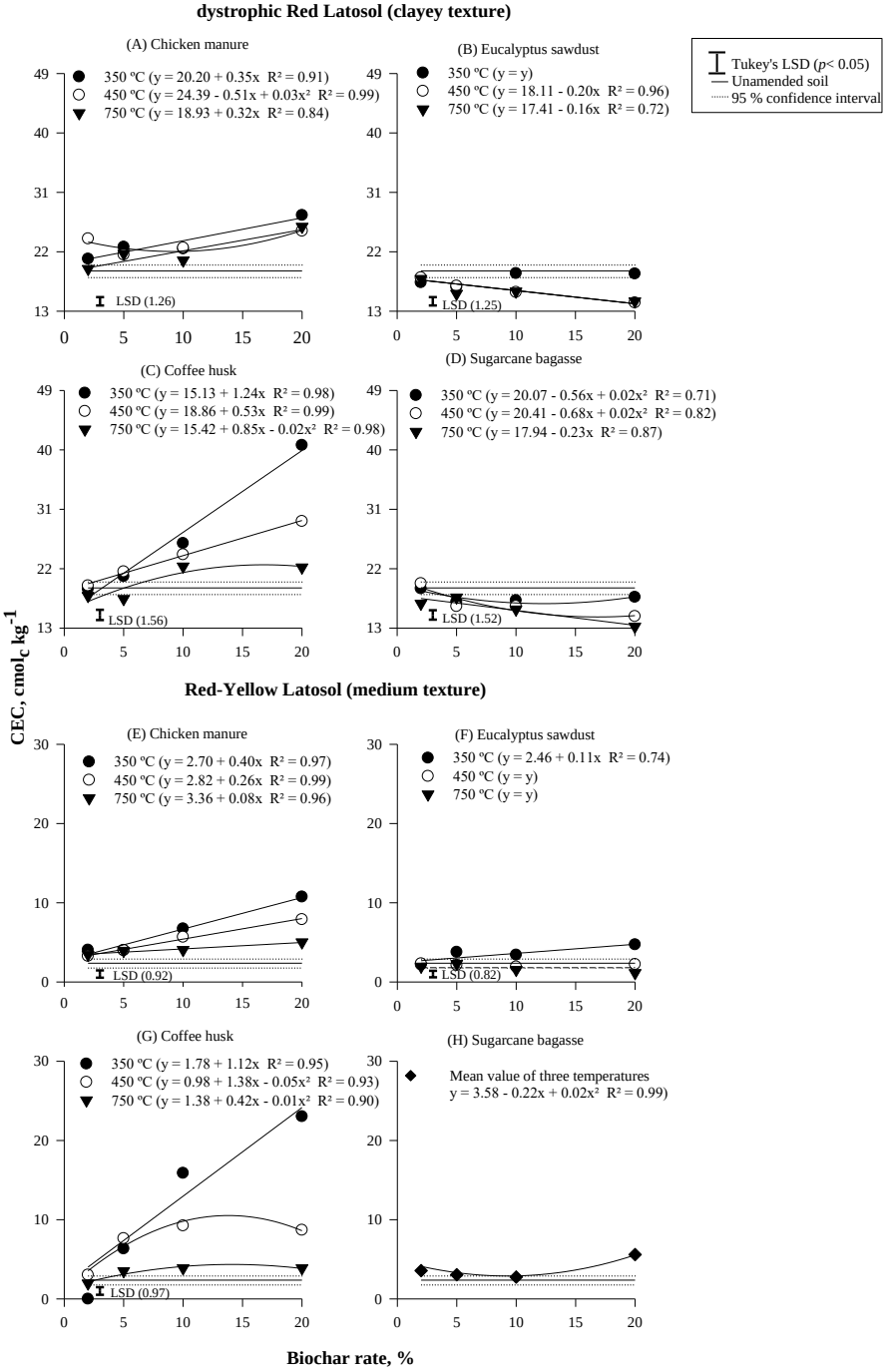

Figure 1. The CEC of the RedLatosol (clayey texture) and Red-Yellow Latosol (medium texture) as a function of biochar rates of chicken manure (**A**,**E**), eucalyptus sawdust (**B**,**F**), coffee husk (**C**,**G**) and sugarcane bagasse (**D**,**H**) pyrolyzed under different temperatures, after 9 months of incubation. Tukey's Least Significant Difference (LSD) ($p < 0.05$).

The highest increase in CEC was observed for the soil amended with CH biochar at 350 °C, which differed from the other pyrolysis temperatures at the highest biochar rate (Figure 1C,G). In the Red Latosol, the addition of 20% CH350 biochar roughly doubled the soil CEC (from 19.1 to 40.4 $cmol_c$ kg^{-1}) (Figure 1C), while in the Red-Yellow Latosol, the same treatment increased the soil CEC by ten-fold from 2.3 to 23.1 $cmol_c$ kg^{-1} (Figure 1G). Despite the high rate (20%), it was possible to achieve a high CEC with a single application, surpassing even CEC values measured in Amazonian TPI soils [50,51]. The positive effect of adding CH350 to soils was hypothesized due to

the high CEC of these charred matrix (70 $cmol_c$ kg^{-1}, Table 1), which was the combination of low pyrolysis temperature and an ash-rich feedstock. Similar results were already reported by other authors [30,52]. The high CEC observed for CH biochar is possibly due to the high K content in the feedstock, which during pyrolysis can intercalate and cause the separation of carbonaceous lamellae by the oxidation of cross-linking C atoms [29]. According to Veiga et al. [53], compared to wood biomasses, coffee husk has greater lignin, ash and fixed C contents, which contribute to its higher thermal stability evidenced by thermal gravimetric analysis. The presence of K in the feedstock alters C degradation due to a greater thermal stability of organic compounds formed during pyrolysis [54]. In another study, the addition of 15 t ha^{-1} coffee husk biochar (pyrolyzed at 500 °C) in an acid soil also increased the CEC from 24.9 to 34.9 $cmol_c$ kg^{-1} after three months of incubation as a result of the high CEC of the biochar (79 $cmol_c$ kg^{-1}) [37]. For both clayey and medium texture soils used in this study, the CEC values are the highest already reported for Brazilian weathered soils. With this perspective, it may be possible to create in the short-term an artificial black earth soil with a high capacity to retain cations in exchangeable forms, and even with a greater CEC than those values reported for the most fertile Brazilian Indian black earths [8]. However, to increase the soil CEC and avoid soil alkalization, the application rate of CM and CH-derived biochars should not exceed 2% (*w*/*w*), regardless of the pyrolysis temperature. Accordingly, to increase the soil CEC with high rates of CM and CH biochars, both materials need to be neutralized prior to soil application, otherwise both Oxisols will be alkalinized, and the fertility of these typical tropical soils will not be improved.

The addition of CH750 only had a minor impact on the CEC of both soils evaluated in this study (Figure 1C,G), which reflects the reduction in the CEC of biochars prepared at high pyrolysis temperatures, possibly, due to the loss of oxygenated functional groups during pyrolysis [17,55–57]. Additionally, CEC could be reduced due to the conversion of carbonate species (i.e., $CaCO_3$) into oxides (CaO) [54]. Although CH450 has CEC values (Table 1) and functional groups (Figure 1C) like those observed in the CH350, its effect on soil CEC was lower than that of CH350 (Figure 1C,G). The dissimilar effect of CH350 and CH450 on soil CEC can be linked to the thermal stability of ligno-cellulosic compounds. Approximately 75% of the original cellulose mass remains in matrices heated at temperatures up to 350 °C, whereas from 330 to 430 °C, the cellulose decomposes rapidly, reducing to only about 15% of the original compounds as estimated by thermal decomposition [58,59]. Consequently, the higher content of cellulose could stimulate a greater microbial activity, potentially leading to the oxidation and formation of new functional groups in the structure of the biochars incubated in soil (e.g., biochar "weathering") [8,9,60].

CM350 also increased the soil CEC with increasing application rates, reaching values up to 27.5 $cmol_c$ kg^{-1} in the Red Latosol, and 10.8 $cmol_c$ kg^{-1} in the Red-Yellow Latosol. The high temperature biochar also caused a significant increase in the soil CEC, even though this increase was slightly lower than that observed for low pyrolysis temperature biochars (Figures 1E and 2A). As for the CM biochar, the intensity of organic functional groups in the biochars by FTIR spectra remained largely unchanged, regardless of the pyrolysis temperature [28]. Protection of organic groups, even at high pyrolysis temperature, may be associated with the high ash content found in CH and CM feedstocks (Table 1). The elemental components in ash could act as catalysts for carbonization reactions [61] or even altering the thermal energy transfer [54], which may protect organic compounds against degradation, and may hinder the formation of aromatic structures as charring intensity advances [62].

There was a linear decrease in the CEC of the Red Latosol with increasing application rates of ES and SB biochars (Figure 1B,H). The soil CEC reduced gradually from 19.1 $cmol_c$ kg^{-1} (unamended soil) to a minimum of 14.3 and 13.2 $cmol_c$ kg^{-1} when the soil was amended with 20% ES750 and SB750, respectively. In the Red-Yellow Latosol (medium texture), there was a slight increase in the CEC after the application of ES350 and SB at all pyrolysis temperatures, with values of 2.36 and 3.23 $cmol_c$ kg^{-1} above the control, respectively (Figures 2B and 1H). Such results can be explained due to the dilution effect at these high biochar application rates, since the CEC of these biochars (ES and SB) is lower than those of the soils. Similar results were observed by Schulz and Glaser [63], considering that soil CEC

was not increased by wood biochar addition. Although the length in this study is longer than other short-term incubation studies with biochar [10,39,64–67], it was not long enough to cause oxidation on the surface structure of the studied biochars. Such an effect would take long periods under field conditions for reactions to occur as was hypothesized for the Terra Preta soils [51]. This is the reason why it is important to tailor the biochar prior to its application to improve key soil properties and benefits to crops from the short-term use of charred matrices.

3.3. Soil C

Total soil C increased linearly over biochar addition rates in both soils. Furthermore, except for the CM treatments, the total C increased over increasing pyrolysis temperature (Figure 2). High temperature biochar is characterized by a high degree of polymerization, leading to a more condensed C structure in the biochar [12]. The larger number of aromatic structures increases the resistance of the biochar to microbial degradation, increasing the persistence of its derived C in soil [10,21]. This supports the assumed low mineralization rates of charred C even after 9 months incubation of the soil–biochar mixtures.

The highest increase in soil C content was observed for soils amended with ES biochar (especially for ES750), compared to the other biochar types (Figure 2B,F). In the Red Latosol (Figure 2B) and Red-YellowLatosol (Figure 2F), the total C contents were, respectively, 13.2% and 18.6% for ES750 at 20% addition rate, which is 3.1 and 11.2 times greater than the C content of control. In the Red Latosol amended with CH and SB biochars, the total C reached a maximum of 14.0% and 16.9%, respectively. As for the Red- Yellow Latosol, the highest values of C were 10.9% (CM) and 12.6 % (SB). Compared to other biochars, the CM-derived biochar was not as effective as other biochars in increasing soil total C content (Figure 2A,E). Increase in soil C contents was preferentially driven by C input from the added biochar rather by the variation of clay and OM contents of soils. The C contents reported in this study for the low-ash (SB and ES) biochar-amended soils are possibly the highest already reported for non-flooded and artificially managed soils found in the warm and rainy Brazilian landscape, considering the C contents already reported for soils of the "cerrado" biome of Minas Gerais [68].

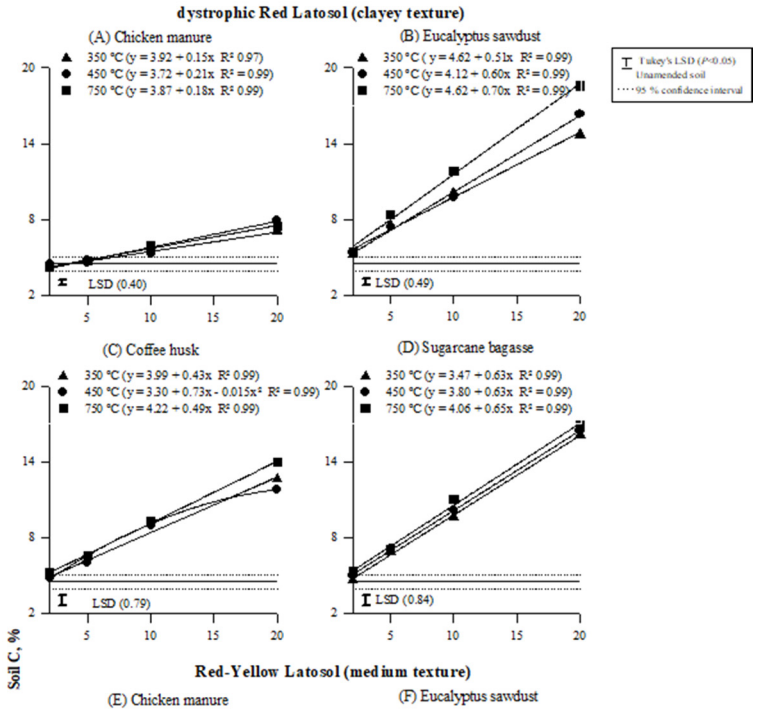

Figure 2. *Cont.*

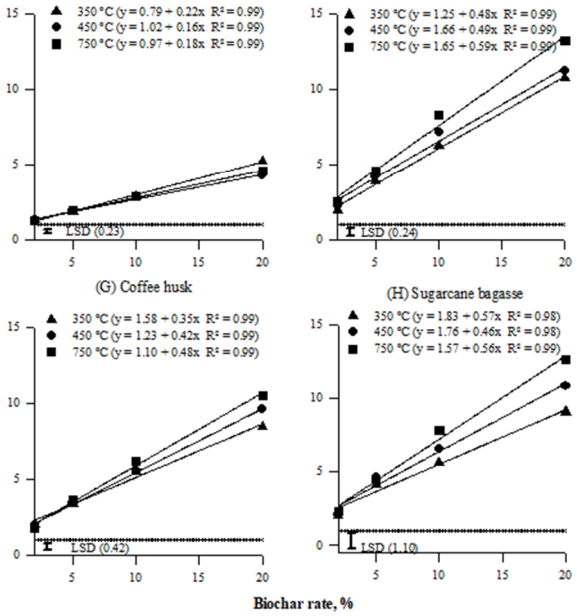

Figure 2. The total C of the Red Latosol (clayey texture) and Red-Yellow Latosol as a function of biochar rates of chicken manure (**A**,**E**), eucalyptus sawdust (**B**,**F**), coffee husk (**C**,**G**) and sugarcane bagasse (**D**,**H**) pyrolyzed under different temperatures, after 9 months of incubation. Tukey's Least Square Difference (LSD) ($p < 0.05$).

3.4. Soil pH

The soil pH increased significantly in both soils (Red Latosol and Red-Yellow Latosol) with the addition of all biochars, after 9 months of incubation (Figure 3). Soils treated with CM and CH biochars showed markedly the highest soil pH (compared to the other biochar treatments), which correlated positively with the increasing biochar rates (Figure 3A,C,E,F). The pH of the Red Latosol increased from 3.4 to a maximum of 7.4 (CM at all temperatures) and 9.2 (CH750). The maximum pH values of the Red-Yellow Latosol were 9.2 (CM750) and 10.0 (CH750), which were significantly higher than the pH of control (4.6). This pH increase is consistent with the alkali compounds and liming value of these biochars (Table S1). Cations such as Ca, Mg, and K contained in large quantities in some feedstocks are converted into oxides, hydroxides, and carbonates, which are concentrated in the ash fraction of the biochar, mainly in those produced at high pyrolysis temperature [66]. The solubilization of these alkaline substances makes biochars function as a liming agent when applied to soil [41,56]. According to Sigua et al. [69], the treatment of a highly weathered soil with a mixture of pine chips and poultry litter biochar increased the pH from 5.9 to up 8.4, as well as improved the soil fertility status. After a 65-day incubation study, the use of plant-derived biochars increased the pH and exchangeable cations and reduced the readily available Al contents of strong acidic tea soils [67]. In an acidic Ultisol (pH 4.3), the use of legume straw-derived biochars, compared to the non-legume-derived ones, was more effective in increasing the pH and base saturation while reducing the toxic levels of exchangeable Al^{3+} [39]. Similar results were observed for the pH values of the biochar-amended soils investigated in this study.

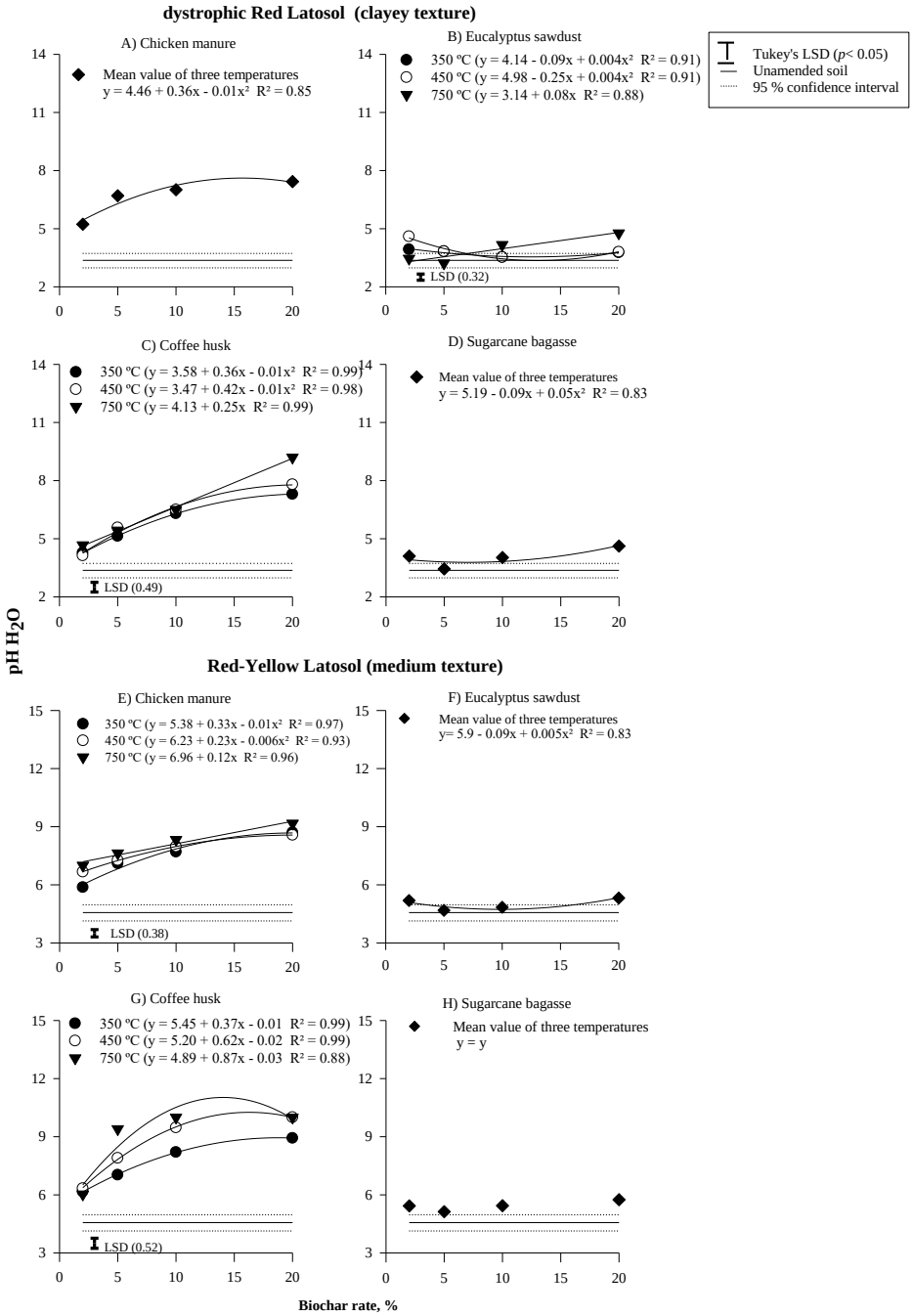

Figure 3. The pH of the dystrophic Red Latosol (clayey texture) and Red-Yellow Latosol (medium texture) as a function of biochar rates of chicken manure (**A**,**E**), eucalyptus sawdust (**B**,**F**), coffee husk (**C**,**G**) and sugarcane bagasse (**D**,**H**), pyrolyzed under different temperatures, after 9 months of incubation. Tukey's Least Significant Difference (LSD) ($p < 0.05$).

The lowest values of pH were observed for both soils amended with ES and SB biochars (Figures 3B and 4D,F,H). In these cases, the pH reached maximum values of 4.8 (ES750) and 4.6 (SB, regardless of pyrolysis temperature), being only slightly greater than the pH of Red Latosol control (Figure 3B,D). In the Red-Yellow Latosol, the pH was not significantly influenced by pyrolysis temperature. In fact, pH increased from 4.6 (control) to 5.3 and 5.8, respectively, for ES and SB at the highest biochar addition rate (Figure 3F,H).

3.5. Modelling the Effects of Biochar on Soil CEC

Changes in soil CEC caused by biochar additions are the direct result of the high CEC values of some biochars, which are from a combination of feedstock properties and extent of charring conditions (e.g., pyrolysis temperature). Anthropogenic soils (Indian Black Earth) of the Amazon region have almost double the CEC of adjacent soils from the same parent material, which is majorly attributed to high C charge density of pyrogenic-derived and functionalized organic matter [51]. It was shown by Cunha et al. [70] that the CEC of anthropogenic soils was strongly correlated to the humin C fraction (stable fraction) and total C, possibly inherited from added charred materials. Interestingly, in this study, the CEC did not correlate with total C in biochar-amended soils (Table 3).

Table 3. Pearson's correlation coefficient calculated for the whole dataset of C contents and pH as related to CEC of each biochar-amended soil.

Soil Property	Pearson's CorrelationCoefficient (R)	
	CEC—Red Latosol	CEC—Red-Yellow Latosol
Total C	−0.162 ^{ns}	0.149 ^{ns}
pH	0.705 *	0.529 *

Notes: ^{ns} non-significant; * statically significant at $p \leq 0.05$.

Furthermore, the increase in soil C by biochar addition did not explain the increase in soil CEC, which is demonstrated by the low coefficient of correlation observed for both soils (Table 3). This can be verified in the treatments with C-rich biochars (ES and SB), which increased the C content but did not alter the CEC. In some situations, the addition of some biochars even caused a reduction in the soil CEC due to the dilution effect at high addition rates (Figure 3).

In each soil, pH significantly correlated with soil CEC for all biochar types and rates tested. The highest correlation coefficient for soil pH and soil CEC was observed for the Red Latosol. This is due to the high native content of soil C, as well as the influence of pH on the density of negative charges on organic colloids. Cation exchange capacity is strongly pH-dependent on tropical soils and some alkaline biochars can raise the soil pH and, consequently, the soil CEC [32,56,71], with a concomitant contribution of the biochar CEC itself [35]. In a soil acidified by the excessive use of N fertilizers, the use of peanut shell-derived biochar (300–400 °C) increased the pH, CEC, SOM, as well as the maize biomass by 15–33% [72].

The observed increase in the CEC of soils by the addition of CH and CM biochars was a result of the high CEC of these matrices, as well as their high liming values. Available data suggest that the intrinsic CEC of biochars is consistently higher in high-ash than in low-ash biochars [43,73]. During the conversion of feedstock into biochar at low pyrolysis temperatures, elements such as Mg, K, Na, and P are able to catalyze the formation of oxygenated surface groups in the edge of the biochar matrix [74], with the subsequent formation of carboxylic, lactones and phenols, which contribute to the increase in biochar density of negative charges. However, negative charges of biochar surface groups may be sharply reduced with increasing pyrolysis temperature [33]. Therefore, the high concentration of K in CH feedstock could be the reason for the high potential CEC of CH biochars pyrolyzed at low temperatures (350 °C and 450 °C) [28].

To predict the changes in soil CEC due to the addition of different biochars, linear regression models are presented in Table S2. The results for the comparison between observed and predicted soil CEC are shown in Figure 4. As seen in Figure 4, there is good predictability of the soil CEC based on this model.

The results shown in Figure 4 indicate that the final soil CEC can be predicted theoretically by the original CEC of the biochar and soil. Although biochar oxidation and functionalization in the Oxisol richer in C and clay content might be expected, the results of this study suggest that there is only a minor change of CEC in soil due to biochar aging in this short-term incubation study. These results suggest that CEC created in some biochar–soil mixtures are derived from the original biochar feedstock,

the extent of pyrolysis conditions, biochar CEC, and its amendment rate and, as a minor factor, the effect of biochar in neutralizing the soil acidity. With progressive aging, the biochar surface is believed to be enriched with functional groups such as carboxyl, phenolic, and carbonyl while oxonium groups are reduced and pyrydine and pyrydone groups are transformed [19]. However, biochar aging is not expected to occur within short-term studies, as biochar oxidation is slow in natural ecosystems [15].

Since the CEC of native soil organic components are greater than that of low-ash and wood biochars, biochar application in acidic sandy soils with low C contents will have neglectable impact, unless biochar oxidation significantly occurs with time [35]. High availability of dissolved organic matter in soils or in the biochar matrix could also stimulate microbial activity, contributing to accelerated biochar oxidation [34]. In a long-term field incubation study (5 years), Dong et al. [75] reported that mass loss of biochar mixed with an agricultural soil was nearly 40%, although only slight chemical structural differences were observed for the aged and fresh biochars. In our study, there were only minor losses of C from biochar in soil during the incubation, especially in the Red-Yellow Latosol (Figure 2), where the predicted CEC are correlated with the observed CEC. In the case of both Oxisols (Figure 4), there was some variation of soil CEC that could not be fully predicted by the model. The use of the whole dataset (soils combined) improved the CEC prediction. As far as we are aware, this was the first attempt to develop a decision support tool for predicting the soil CEC increase in response to biochar addition in weathered contrasting soils. The modelling approach used in this study is useful to forecast whether biochar addition will result in positive, negative or neutral effect on soil CEC as a function of the inherent soil CEC and biochar CEC, as well as the biochar rate rather than the biochar liming effect on the final soil pH.

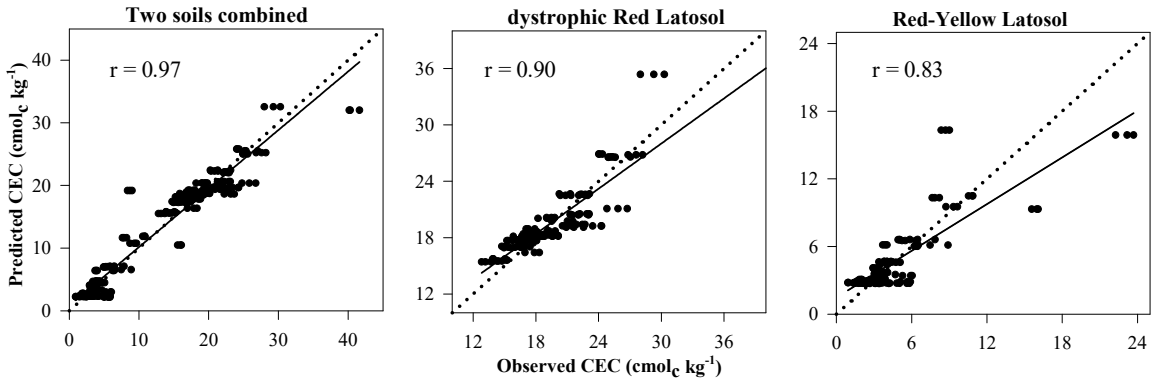

Figure 4. Cation exchange capacity (CEC) predicted by Equation (1) (soil CEC = a + b CEC *biochar weight* + c CEC *soil weight*) and CEC determined by the sodium acetate method.

3.6. Agronomic and Environmental Implications and Future Guidelines

The results of this study showed that the use of high-ash biochar (pyrolyzed at 750 °C) can alkalinize the Oxisols. Even at low application rates, alkalization of soils treated with high-ash biochars such as those derived from CH and CM can occur, representing a potential constraint on soluble P forms, cationic micronutrient availability, and increased volatilization of N as ammonia, mainly in the low-buffered middle texture soil. Therefore, the recommended rate of biochar to increase soil CEC should be based on the capacity of the charred matrix to alter pH levels below the threshold limit for most crops. For this reason, the addition rates of CM and CH-derived biochars, regardless of the soil incubated, must be ≤2% (*w*/*w*). Alternatively, low-ash/wood biochars, regardless of the rate added to Oxisols, are more suitable to store C without causing soil alkalization, though they are not effective in improving CEC. The addition of naturally or artificially oxidized [19] high-ash derived biochar pyrolyzed at low temperatures could effectively increase the capacity of soil to retain nutrients and crop yield, while serving as suitable matrices to increase the C stored in soils. Pyrolysis conditions and oxidation pretreatments of CH and CM feedstocks with phosphoric or sulfuric acids to produce high-agronomic value biochars should be performed to increase the benefits of these charred matrices

on soil CEC without increasing soil alkalinity. Apart from the impact on soil CEC reported in this study, the use of functionalized, aged and high-CEC biochars could also represent a suitable way to increase availability of water for crops and the biota activity in drought-affected soils [76]. Moreover, the use of high rates of ash-enriched biochars with the subsequent alkalization of soils could be a management practice to decrease metal leaching from heavy metal contaminated soils. Finally, in line with Glaser et al. [8], the use of some of ES and SB-derived biochars is a suitable practice to increase C concentration in weathered Brazilian soils, though they are ineffective in increasing pH and CEC. Alternatively, CH an CM are potentially matrices to increase the C content, CEC and soil pH, but their use for these purposes is limited by a sharp increase in soil pH to levels beyond those adequate for plentiful crop growth. Regardless of the Oxisol investigated, to improve the fertility of typical low CEC, acidic and poor nutrient tropical soils, high ash-biochars pH must be adequately pretreated in order to increase CEC without causing soil alkalization. CH biochars can supplement imported and expensive K fertilizers used in Brazil, while P from CM biochar can supply part of the P required by crops [28]. In that direction, high-ash biochar added to soil at low agronomic rates at the bottom of furrow in band can act as sources of K (CH biochar), or K, P and Ca (CM biochar), while correcting soil acidity in the zone adjacent to plant roots.

The challenge is to mix biochars that combine the right pH and the capacity to increase the storage of persistent C in soils, as well as the levels of nutrients (such as Ca, P and K). However, to achieve this goal, it is necessary to optimize the pyrolysis temperature, select the right feedstock, and mix compatible biochars to avoid soil alkalization. The preconditioning of biomass to create near neutral and high-CEC biochars is also an option to improve soil CEC without causing alkalization. These actions can improve the use of biochar as a technology to enhance soil fertility of most Brazilian crop fields and biomes. Functionalization through pre- and post-pyrolysis treatments of ES and SB feedstocks and their derived biochars is another strategy to improve soil CEC and the persistence of charred C in soil.

4. Conclusions

Feedstock, pyrolysis temperature and amendment rate are key factors controlling the CEC of biochar-amended soils and C stored in the two Oxisols. High-ash biochars produced at low pyrolysis temperatures (≤ 450 °C) are effective in increasing CEC without improving the Oxisols fertility status. Interestingly, an increase in soil CEC relies on biochar CEC and rate rather than alterations in soil pH. Low-ash biochars (ES and SB) are effective at increasing C storage in soils without causing alkalization. CEC of the amended soils can be predicted from the biochar CEC, addition rate, and the original soil CEC. In this short-term incubation study, aging is a minor factor controlling CEC of the biochar-amended Oxisols. To avoid soil alkalization, the pH alteration in biochar-amended soil is a key property to define the maximum application rate of high-ash biochars.

Overall, this study provides results that guide the tailoring and selecting biochars for specific agronomic and environmental applications, such as improving soil CEC. The combined use of high and low-ash biochars may accomplish apparently conflicting goals such as the simultaneous increase in soil C storage and CEC without causing negative pH effects to plants, nutrients and microbial soil processes.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4395/10/6/824/s1, Table S1: Liming value of the biochars produced from four feedstocks pyrolyzed at 350, 450 and 750 °C. Table S2 Linear regression mathematical models used to predict the final CEC of biochar-amended soils, using as predictors biochar CEC and mass added to soil, soil original CEC and mass, and, when pertinent, net pH (delta pH of the pH biochar treated soil over pH of control soil).

Author Contributions: C.A.S. and M.A.S.-M. conceptualized the research; C.A.S., M.A.S.-M. and R.R.D. designed the research project; R.R.D. performed the study in controlled conditions; R.R.D, C.A.S, P.F.T., M.N.V. and L.C.A.M. analyzed the data; the manuscript was written by R.R.D., M.A.S.-M., L.C.A.M., K.A.S., and C.A.S; All authors have read and agreed to the current version of the manuscript.

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