https://dx.doi.org/10.21577/0103-5053.20220076

J. Braz. Chem. Soc., Vol. 33, No. 12, 1402-1413, 2022
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Article

Interaction of Lead and Calcium with Biochar Produced from Cassava Waste: Perspectives for Agricultural and Environmental Application

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Biochar from slow pyrolysis under controlled conditions is favorable in the transformation of waste into materials that serve as soil conditioners, and/or environmental remediation. Thus, this work aimed to produce and characterize biochar from cassava waste under different temperature conditions and evaluate interactions with Ca^{2+} and Pb^{2+} for agricultural and environmental applications. To investigate the efficiency of the interaction of biochar with nutrients (Ca) and contaminants (Pb), the influence of pH and contact time were evaluated. There was an increase in pH, pHzpc (zero point charge), and condensed aromatic structures in BC, due to the increase in pyrolysis temperature. Also, biochar demonstrated a Pb^{2+} adsorbed amount of 2.03 to 2.37 mg g^{-1} and a Ca^{2+} release capacity of 0.655 to 0.765 mg g^{-1}. In this way, biochar produced from residues of cassava waste can be a viable strategy to enhance agricultural production and reduce environmental contaminants.

Keywords: pyrolysis, contaminants adsorption, nutrients release, soil conditioner, residues reuse

Introduction

The development of Brazilian agriculture and agribusiness is one of the main sectors responsible for the country's economic and social growth. This development leads to a significant increase in the waste generated during the process of production and industrialization, which may cause soil and water contamination when improperly disposed.[1,2]

Brazil is one of the main cassava producers in the world. However, the process of obtaining products from this culture brings concern about a large amount of waste generated. According to Schwantes *et al.*,[3] Brazil produces about 1 million tons of cassava waste (CW) *per* year, and worldwide the figures are approximately 11 million tons. In addition to waste, inadequate management practices may cause environmental and economic impacts. In this sense, looking for strategies to increase the added value of these residues and apply them in environmental remediation and/or in agricultural production is of scientific, economic, and social interest.

Biochar (BC) can be defined as the result of the thermal decomposition process of organic vegetable residues and combustion pyrolysis in conditions of absence or low oxygen concentration.[4] They are formed mainly by carbon, with fine granularity, being resistant to decomposition[4-7] and is discussed by the scientific community as an alternative for the use of these agro-industrial residues.[4,5] BC in these pyrolysis conditions usually has a carbonaceous molecular structure arranged in a disorganized manner, consisting of flat layers of aromatic rings randomly linked, and inorganic composition formed by metals from the raw material.[8] Also, the chemical surface of the BC can have different properties, as hydrophobic, hydrophilic, basic, and/or acidic, contributing to its reactivity.[4]

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Editor handled this article: Fernando C. Giacomelli

The interest in the use of BC is related to its benefits, since to its production there is stable carbon storage, avoiding the action of microorganisms and the release of gas into the atmosphere; in addition to being considered an effective and low-cost product.[9,10] Besides, the application of BC in agricultural soils has the ability to act in waste management, water retention, fertility, and improve the physical, chemical and microbiological structure of the soil.[11]

Thus, the BC applied to soils can be an effective alternative to reduce the bioavailability of potentially toxic elements,[12] improve crop fertility and productivity, contributing to agricultural practices.[13] Also, BC has been used as an adsorbent in the process of remediation of natural and wastewater.[14-16]

The results found in studies[11-16] with BC demonstrate its potential to act in areas considered strategic. In this sense, the production of BC from CW is of scientific interest and promising results have been reported,[17-19] such as in management of residues, production and characterization of BC, chemical modification of BC and interaction with antibiotics and simultaneous adsorption with ions in aqueous solution.

However, it is still necessary to better understand the process involved in the production and performance of BC from CW. In this sense, the results presented in this research show, for example, the best pyrolysis conditions in the production of BC from CW, the influence of the pyrolysis temperature and its relationship with the presence of functional groups that strongly contribute to the process of interaction with metal ions, in addition to demonstrating the ability to act in the interaction with contaminant and nutrient, which in turn, contribute significantly to previous research[4,11] and improves the understanding of the development and more efficient application of BC.

In this context, this work aimed to produce and characterize the biochar from cassava waste in different conditions, and to evaluate its interaction with nutrient (Ca^{2+}) and contaminant (Pb^{2+}), seeking the production of materials that can be used in the remediation of environmental and/or agricultural applications.

Experimental

Reagents and solutions

All reagents used were of analytical grade and acquired through Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, USA). All solutions were prepared with ultrapure water obtained from a Gehaka system (São Paulo, Brazil) with 18.2 MΩ cm (at 25 °C). Before use, all working materials were previously washed with 10% (v/v) HNO_3 and ultrapure water. For nutrient and contaminant studies, standard solutions of the chemical elements were prepared by dilution of commercial stock solutions of 1000 mg L^{-1} (Merck, São Paulo, Brazil) and subjected to pH adjustments for 4, 6, and 8.

Production of biochar from cassava waste

Cassava waste (CW) was collected from Junqueiro City, Alagoas State, Brazil. The waste was air dried, cut in small pieces in a Willy knife mill (Macro, Solab, Piracicaba, Brazil) to obtain homogeneous samples used in the pyrolysis. The pyrolysis of the CW samples was carried out in a laboratory unit consisting of tubular oven JUNG, LT6 of 1 kW (Blumenau, Brazil) heated by electrical resistances with a maximum capacity of 1000 °C, with a cooling system for the collection of the liquid phase. The experiments were carried out keeping the heating rate fixed at 10 °C min^{-1} and resistance time of 90 min. The pyrolysis temperatures were 350 °C (BC1), 450 °C (BC2), 500 °C (BC3), and 550 °C (BC4). After the BC production, the material was cooled to room temperature (25 ± 1 °C), crushed by using a porcelain mortar and pistil, and separated granulometrically in a mesh 42 sieve (< 355 µm).

Characterization of biochar from cassava waste

The physical and chemical properties of BC were investigated. For the thermogravimetric analysis (TGA), 10 mg of the CW sample were subjected to a temperature range of 30 to 900 °C, with a heating rate of 10 °C min^{-1}, in a Shimadzu, DTG-60TG (Tokyo, Japan), simulating pyrolysis conditions.[20] The efficiency of BC sample was obtained from the calculation of the mass variation, in triplicate, by using the equation 1:

$$BC = \frac{M_{final}}{M_{initial}} \times 100 \quad (1)$$

where BC is the mass of the biochar (g), $M_{initial}$ is the initial mass (g), and M_{final} is the final mass after the pyrolysis process (g). The functional groups of the samples were detected using Fourier transform infrared spectroscopy (FTIR), in a Varian spectrometer, 660-IR (Berlin, Germany), with a resolution of ± 4 cm^{-1} in the region of 4000 to 400 cm^{-1}.[21] X-ray diffractograms were obtained with Cu Kα radiation, 40 kV voltage, 40 mA current, scanning region of the diffraction angle from 5° to 40° (2θ) and scanning speed of 0.2° min^{-1}, in a Shimadzu diffractometer, XRD-6100 (Tokyo, Japan).[22] The pH value of the BC was measured by adding the BC to deionized water in a mass ratio of 1:20.[23] The zero point charge (pHzpc) were obtained by Rajkovich methodology.[23]

Interactions between biochar, nutrient and contaminant

The adsorption studies were carried out with samples of BC produced at the temperatures of 350, 450, 500 and 550 °C, in interaction with the nutrient Ca^{2+} and the contaminant Pb^{2+}. A solution of 10 mg L^{-1} of the nutrient and contaminant were added to the BC.

To evaluate the influence of pH on BC adsorption, experiments were carried out at different pH values (4, 6, and 8) using a constant concentration of adsorbate, Ca^{2+} and Pb^{2+} at 10 mg L^{-1}. To check the influence of the solution/BC contact time, the time intervals of 5, 10, 30, 60, 120, 240, 1440, and 2880 min (48 h final) were used. Aliquots of 12 mL of the metal solutions prepared at different pH values were added in conical tubes containing 50 mg of BC samples, which were kept under mechanical agitation (100 rpm) at 25 ± 1 °C at different time intervals. After these intervals, the solutions were filtered through 0.45 µm porosity membranes (Millipore, Massachusetts, USA). The released nutrient and the adsorbed contaminant were determined by microwave plasma atomic emission spectroscopy (MP-AES).

The values of Ca^{2+} and Pb^{2+} adsorbed/desorbed in BC samples were calculated from the difference between the initial and final concentrations of the solution, using equation 2:

$$q = \frac{(C_o - C)V}{m} \quad (2)$$

where q is the adsorbed amount of Pb^{2+} and Ca^{2+} ion (mg g^{-1}), C_o and C (mg L^{-1}) are the initial and final metal ions concentration, respectively. V is the volume of the solution (L), and m is the mass of BC (g).

To investigate the possible mechanisms of interaction between nutrients/contaminants and adsorbents, a pseudo-first order model[24] and a pseudo-second order model[25] were applied.

The pseudo-first order model was proposed for adsorption of a solid-liquid system, being indicated to determine the adsorption rate of a given solute in a liquid solution. However, for experiments that extend over longer times, the equation that represents the pseudo-first order model does not show good results.[26] The pseudo-second order model can be applied to study kinetic behavior without restriction regarding the time of balance.

In this sense, the linearized equations used to adjust the kinetics data were pseudo-first order (equation 3) and pseudo-second order (equation 4):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_t} \quad (4)$$

According to the equations presented, q_e is the amount of adsorbate that remained retained on the surface of the solid at equilibrium (mg g^{-1}), q_t represents the amount of adsorbate that was retained at time t (mg g^{-1}), k_1 and k_2 represent the constants for the reaction rate of pseudo-first and pseudo-second orders, respectively, and t is the time (min).

The applicability of the models presented was verified by the graphs $\ln(q_e - q_t)$ *versus* t and t/q_t *versus* t, respectively.

Contents of nutrients and contaminants

The contents of nutrients and contaminants (Al, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sr and Zn) present in CW and BC samples were determined by microwave plasma atomic emission spectroscopy, using Agilent Technologies, 4200 (Santa Clara, USA) after acid digestion.[27,28] The analyses were performed according to the guidelines established by the manufacturer Agilent Technologies.

All reagents used had a high purity degree and the number of trace metals was verified. Analytical calibrations curves were performed using a multi-element standard solution with concentration range 0.010-2.50 mg L^{-1} (Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sr and Zn) and 2.50-20.00 mg L^{-1} (Al) in Agilent Technologies, 4200 (Santa Clara, USA).

Results and Discussion

The effects of the BC are promising in the performance of agricultural practices and waste management, however, for its use, it is necessary to know its properties and how they can interact when applied in the various production and environmental remediation systems. These properties are dependent on the variety and heterogeneity of the raw material used in the production of BC, and also on the pyrolysis conditions.[29]

In this sense, the characterization of BC is essential to elucidate its properties and define the best pyrolysis conditions, which must be appropriate to the interests of the BC application, always seeking the balance between its properties and the destination of the product.

Characterization of biochar from cassava waste

Thermogravimetric analysis of CW helped to elucidate the stability of biomass as a function of temperature, contributing to the definition of the best pyrolysis conditions for BC production aiming at environmental application. The thermal analysis of this study was expressed in the thermogravimetric curve (TG) and its derivative (DTG), used to understand the behavior and characteristics of the thermal decomposition of the biomass of CW (Figure 1).

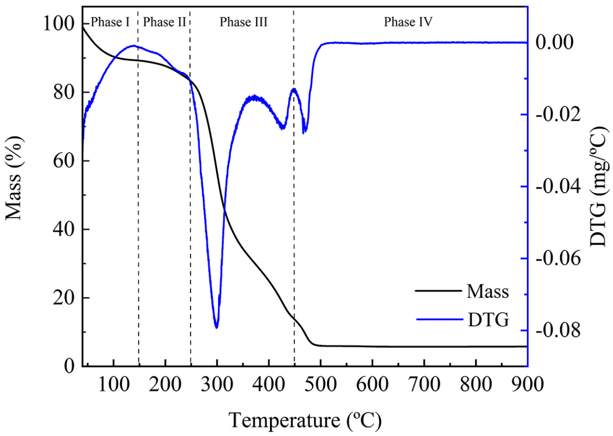

Figure 1. Thermogravimetric (TG) and derivative analysis (DTG) of the cassava waste (CW).

The TG and DTG (Figure 1) showed different phases of decomposition. The first being up to 150 °C, showing 10.7% of loss in mass, corresponding to moisture and adsorbed water and volatile compounds.[30] In the second phase, between 150 and 250 °C, there was a loss of approximately 17% in mass, the main characteristic of the beginning of the decomposition of hemicelluloses and the beginning of the decomposition of cellulose. In the range of 250 to 450 °C, we observed the third phase with rapid kinetics, marked mainly by the decomposition of cellulose and the beginning of the decomposition of lignin, with a loss of approximately 86% in mass. Above 450 °C, we can see the fourth and last phase, in which the decomposition of the remaining lignin occurs, in addition to the other compounds of greater molar mass that make up the biomass, being marked by slow kinetics,[31,32] the main characteristic of carbonaceous materials.[30]

It was also possible to verify that in the range of 250 to 450 °C, occurred the highest rate of mass loss (Figure 1). Seeking a balance between higher yields of the solid phase, recalcitrant characteristics, and conservation of reactive groups in BC, this work focused on temperatures from 350 °C to evaluate the effect of the temperature on the properties of BC and their efficiency.

The BC yield from the pyrolysis process is one of the main factors for the feasibility of the application and performance of this material in the various processes of interactions with chemical species.

The increase in temperature in the CW pyrolysis process led to a reduction in the efficiency and formation of the BC (solid phase). The yield of BC1, BC2, BC3 and BC4 were 36.7, 32.3, 28.3 and 24.6%, respectively. There was a reduction of approximately 12% when it rose from 350 to 450 °C; about 22.9% when the maximum pyrolysis temperature went from 350 to 500 °C; and approximately 33% when the pyrolysis process went from 350 to 550 °C. This reduction in the yield of the solid phase can be attributed to the composition of the biomass, which mainly presents hemicellulose, cellulose, and lignin, characteristics that must be taken into account for its performance as a soil conditioner.[32] Based on the results obtained, about the yield, it is more interesting that the pyrolysis temperature is kept at 350 °C.

FTIR analysis for CW and BC was used to verify if changes in functional groups occurred due to temperature increase during the pyrolysis process of CW (Figure 2). Peaks referring to reactive chemical groups, such as oxygenated groups, and of greater recalcitrance, such as aromatics, in BC (Figure 2b), and absence of functional groups about the raw material (Figure 2a) were observed. The absence of the characteristic peaks present in CW with BCs is attributed to the pyrolysis process, which mainly results in the gradual degradation of various functional groups present in biomass and confirmed by TGA (Figure 1).[32,33]

The FTIR spectrum for the BCs evaluated showed an intense band at 3425 cm^{-1} (Figure 2b), which is associated with the stretching of the hydroxyl group. The band observed at 1625 cm^{-1} can be attributed to the stretching of C=C bonds of aromatic groups. The 1389 cm^{-1} band can be related to the presence of oxygenated groups present in the lignin, weakening the peak with increasing temperature.[33-35]

The presence of oxygenated groups on BC surfaces is an important factor for acting as a conditioner in the soil due to the chelating action of these groups with nutrients, in addition to contributing to water retention and pH control. Also, the presence of double bonds between carbon atoms in aromatic groups provides BC with greater stability when applied to the soil, being less susceptible to the actions of microorganisms and, consequently, it will have greater stability in the environment.[4]

The X-ray diffraction technique (XRD) applied to BC produced from CW (Figure 3) was an important method to evaluate the influence of pyrolysis temperature on the crystallinity and structure of BC, acting as a mechanism in the interpretation of the material. In this way, we were able to assess the degree of condensed aromatic structures

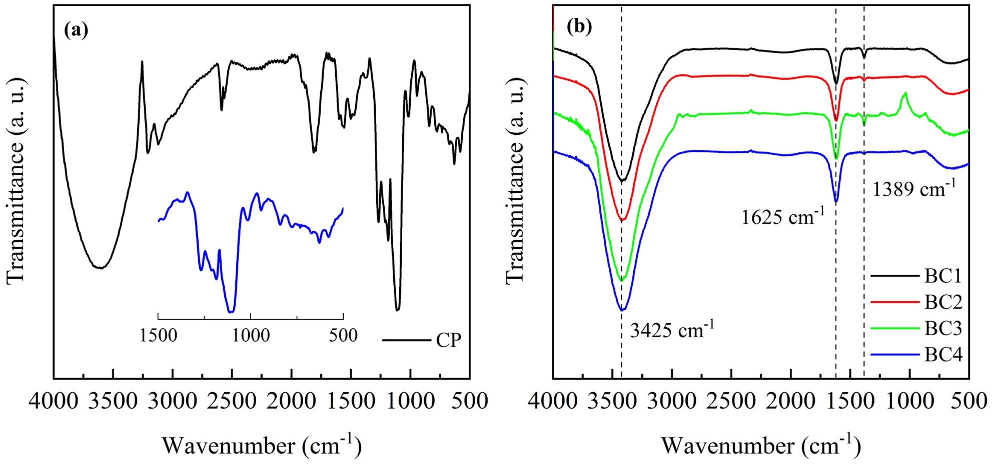

Figure 2. Infrared spectra (FTIR) for (a) cassava waste (CW) and (b) biochar (BC) produced under different temperature conditions: BC1, 350 °C; BC2, 450 °C; BC3, 500 °C; and BC4, 550 °C. The insert in (a) represents values in an increased scale (wavenumber from 1500 to 500 cm^{-1}) for better visualization.

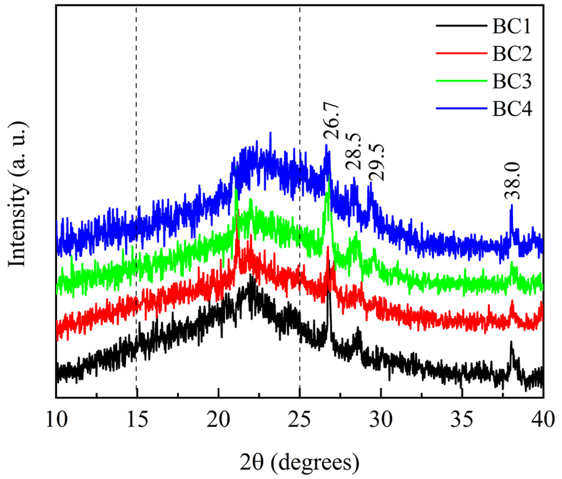

Figure 3. Biochar (BC) X-ray diffraction (XRD) obtained at different pyrolysis temperatures: BC1, 350 °C; BC2, 450 °C; BC3, 500 °C; and BC4, 550 °C.

and, consequently, the potential of the BC to act as an environmental remedy and in carbon sequestration.[4,5]

It can be seen a wide peak in the region of 2θ = 15° to 25°, with a decrease in intensity and pyrolysis temperature increase (Figure 3), showing that the structure of the material is amorphous. However, the decrease in intensity in this region may be related to the decrease in the amorphous phase as the temperature increases, corroborating the percentage of crystallinity of 17.0, 16.9, 21.0 and 26.7% for BC1, BC2, BC3 and BC4, respectively. Still, regarding this peak, our results did not show the peak for cellulose in the region at 2θ = 22.7°, as reported by Regmi *et al.*,[36] which can be related to the crystalline structure of cellulose.[37]

The peak observed at 2θ = 26.7° in all BCs, which showed only a variation in intensity between the BCs analyzed (Figure 3), can be attributed to the presence of silicon dioxide in the soil.[38] Besides, the other peaks observed in all BC at approximately 2θ = 28.5, 29.5, and 38° (Figure 3) may be related to the presence of traces of calcite, dolomite and quartz, respectively.[38,39]

In this sense, the XRD analyses of BC samples indicate that it is not a graphical structure, which is an indicative of cellulose degradation, as can be evidenced in the thermal analyses (TG/DTG curves, Figure 1). In this context, cellulose is discussed as the only component of lignocellulosic biomass that contributes to the crystalline phase, while hemicellulose and lignin contribute to the amorphous phases.[38] The graphical structure in BC would be an important factor when applied to the soil for resisting degradation by the actions of microorganisms for a longer period and, consequently, contributing to the conservation of carbon in the soil and reducing the emissions of gas that favor the greenhouse effect.[4]

Although the physical and chemical structure of BC is influenced by pyrolysis conditions, mainly by temperature, the graphitic structure in BC is achieved by most materials from biomass at elevated temperatures (3500 °C).[40] Thus, in the BC studied, formations of organized structures can be found forming condensed aromatic structures, as evidenced by the FTIR analysis (Figure 2), but without the presence of a graphite crystalline structure.

The BC pH is a very important property for application as a soil conditioner and depends on the raw material and pyrolysis temperature conditions. The BC can change the chemical properties of the soil, such as increasing the pH,[41] contributing to the reduction of acidity and improving the availability of nutrients.[5,41] In this sense, seeking to evaluate the influence of temperature on the pyrolysis process of the CW biomass, the pH of the BC produced was determined (Figure 4).

We observed an increase in pH with an increase in pyrolysis temperature (Figure 4). This increase may be

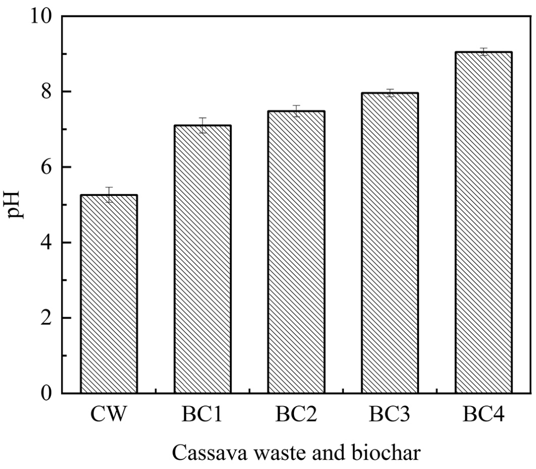

Figure 4. pH of cassava waste (CW) and biochar (BC) pyrolyzed under different temperatures: BC1, 350 °C; BC2, 450 °C; BC3, 500 °C; and BC4, 550 °C.

related to acid groups that are more susceptible to thermal degradation than basic groups.[34,42,43] The increase in soil pH as a result of BC application is evidenced as the main responsible for the increase in crop productivity.[42]

The pH values obtained for CW, BC1, BC2, BC3, and BC4 were 5.26, 7.10, 7.48, 7.96, and 9.05, respectively (Figure 4).

The raw material for the production of BC is an important factor for the role of BC in the correction of soil acidity (liming), since the increase in pH in acidic soils from the application of BC is mainly attributed to the content of alkali metals and alkaline earth metals in the material, such as K^+, Ca^{2+} and Mg^{2+}, which are present in the BC ash obtained during the pyrolysis process. According to Mikan and Abrams,[44] the performance of BC in acidic soil can promote an increase of 0.4 to 1.0 pH units. Therefore, the results of BC produced from CW demonstrate the possibility of acting as a soil conditioner, providing an increase in pH and, consequently, being able to contribute to a significant increase in agricultural productivity.

The pHzpc is an important factor to contribute to the understanding of the effect of pyrolysis conditions on the loads present on the surface of BC and the mechanisms involved in the adsorption process.[45] The variation of the surface load in the BC compared to the raw material (CW) can contribute to adsorption processes to remove cations and anions in different pH ranges.

The pHzpc values obtained for CW, BC1, BC2, BC3, and BC4 were 5.09, 6.98, 7.21, 7.04, and 7.26, respectively. Ribeiro *et al.*[46] report that below pHzpc, material surfaces would be positively charged, favoring interaction with anions, and at higher values than pHzpc, surfaces would be negatively charged, favoring interactions with cations.

Evaluating CW as adsorbent material, in addition to this study, Schwantes *et al.*[47] found pHzpc 6.02, a difference that may be related to factors such as the variety of the crop and the characteristics of the soil and climate in which the crops occurred. Also, the increase in pHzpc in BC can be related to changes in the surface characteristics, being observed by the variation of intensity in the infrared. In this context, the increase in pHzpc found in BC (pHzpc 6.98 to 7.26) concerning that found in fresh material (CW) (pHzpc 5.09) shows that the BC obtained can be favorable both in interactions with anions and interactions with cations, since the pHzpc of BCs are close to pH 7. These characteristics are promising for the application of BCs in adsorption processes of environmental contaminants, contributing to environmental remediation.

Interactions between biochar, nutrient and contaminant

Pb^{2+}

The behavior and effects of lead (Pb) in the environment are influenced by several factors related to speciation, which can be understood as the existence of different chemical forms for a given chemical species under different environmental conditions.[48]

In the distribution of lead species as a function of pH (Figure 5), it is noted that at pH below 6 the lead occurs mainly in the ionic form Pb^{2+}. However, at values above this pH, several chemical species with different charges may be present, such as $Pb(OH)^+$ and the precipitation of lead in the form of $Pb(OH)_2$. Thus, the distribution and fraction of species are important factors to understand the behavior of interactions between species in aqueous solutions and adsorbents.

pH is an important factor that influences the adsorption

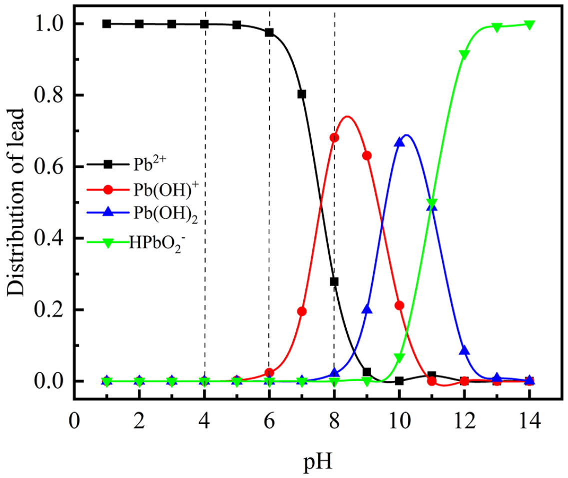

Figure 5. Distribution of lead (Pb) species in aqueous medium as a function of pH using Visual Minteq software.[49] The dotted lines indicate pH 4, 6 and 8, which were used to carry out the experiments.

of metallic species in aqueous solutions since it affects the availability of chemical species that will be in solutions (Figure 5), as well as the activity of functional groups present in the adsorbent material.[50] In this sense, seeking to evaluate the influence of pH and contact time on the adsorption of Pb^{2+} by the BC produced at different temperatures, the adsorption of the contaminant at pH values of 4, 6, and 8, and the profiles of the kinetic curves were evaluated. The rate of adsorption of the contaminant was fast, with 84.79 to 98.92% of this contaminant in BC, expressed by the adsorbed amount (q), occurring mainly in the first 120 min among all evaluated systems (Figure 6).

The pH affected the Pb^{2+} adsorption in BC, being more efficient at pH 4 and 6 for BC1, BC2, and BC3 (Figures 6a, 6b and 6c, respectively) and pH 8 for BC4 (Figure 6d). The study developed by Mohan *et al.*[51] evaluated the adsorption for lead (Pb) and cadmium (Cd) in BC of vegetal origin obtained by pyrolysis, and observed the maximum adsorption capacity in the pH range of 4 to 5, demonstrating a significant interaction capacity of these metallic species in acidic pH intervals.

In this context, the results observed for BC1, BC2 and BC3 may be associated with the competition between protons and metallic cations about the sites on the surfaces of the BCs.[52] At pH 8, the reduction in the adsorbed amount for BC1, BC2, and BC3 to pH 4 and 6 may be related to the reduction of the fraction of Pb^{2+} and the existence of the species $Pb(OH)^+$ and $Pb(OH)_2$ with a similar distribution, with positive and zero charges, respectively (Figure 5).

For the BC4, which was pyrolyzed at the highest temperature (550 °C), there was greater efficiency in removing Pb^{2+} at pH 8 (Figure 6d) compared to the other BC produced at lower temperatures. The adsorbed amount at pH 8 may be related to changes in its properties, including the reduction of surface functional groups by increasing the temperature of pyrolysis and modification of the porous structure. Also, the electrostatic attraction mechanism may promote strong interactions with potentially toxic metals.[5,34,53] Thus, considering the results of pHzpc, with pH 8 > pHzpc for BCs and, consequently, favoring the attraction of cationic metals, the electrostatic attraction mechanisms are probably one of the main means of contributing to the strong interaction between BC4 and Pb^{2+} in this pH range.

The adsorbed amount (Figure 6e) and the percentage of retention (Figure 6f) of lead in the evaluated BCs showed potential for interaction and efficiency in removing the contaminant in an aqueous solution at different pH ranges (4, 6, and 8). This shows that the BC produced

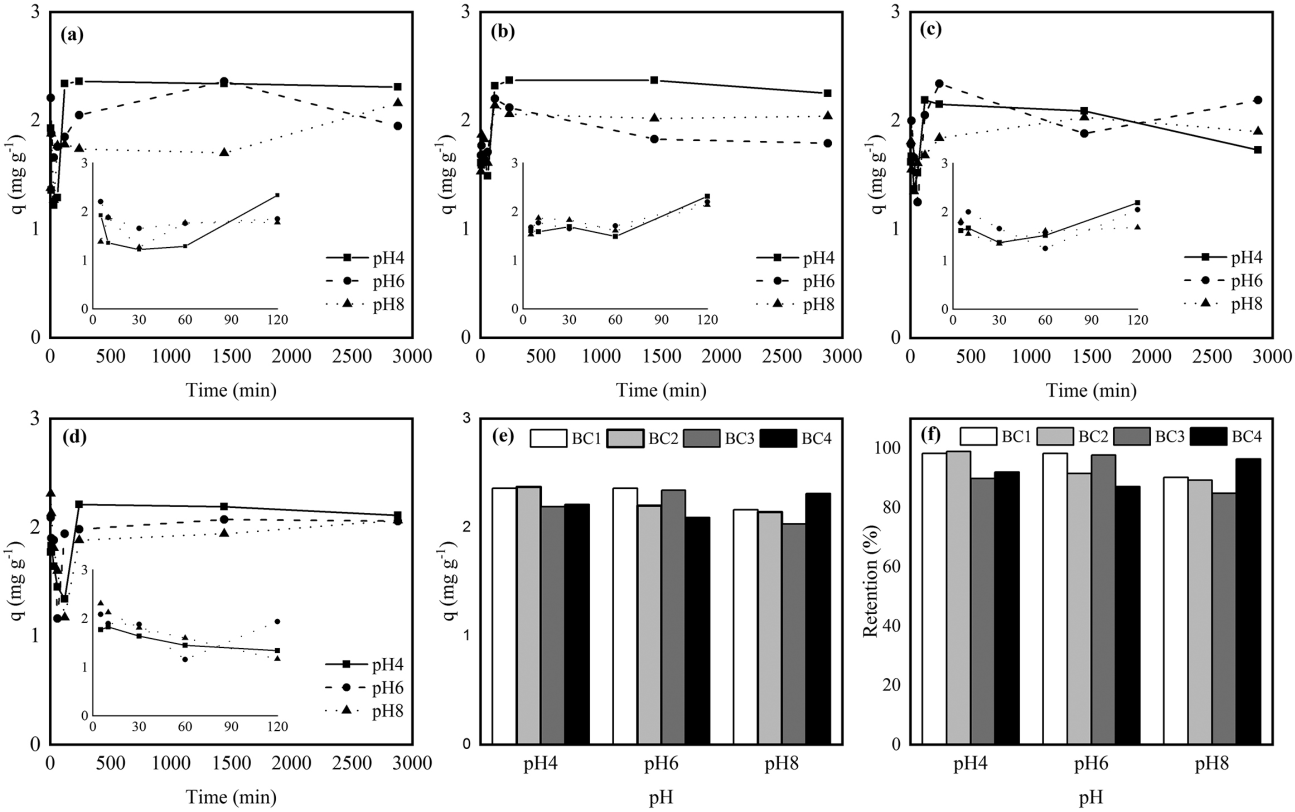

Figure 6. Influence of pH and time on the lead adsorption process: (a) BC1 (350 °C); (b) BC2 (450 °C); (c) BC3 (500 °C); (d) BC4 (550 °C); (e) adsorbed amount; (f) percentage of adsorption produced in different pyrolysis temperature conditions. The inserts in (a), (b), (c) and (d) represent values in an increased scale (time from 0 to 120 min) for better visualization.

by CW biomass can be promising for the removal of Pb^{2+} in solutions, a contaminant that can cause serious environmental and social problems, in addition to adding value to the residues from the agro-industrial process of cassava and contribute to environmental remediation.

The studies of the adsorption models were carried out for pseudo-first order and pseudo-second order. The pseudo-first order model did not present a satisfactory correlation adjustment for the evaluated system (result not shown). This model does not show good results for experiments that last longer than 30 min.[26] The pseudo-second order model, on the other hand, showed good results for the evaluated experiment (Table 1). This model is based on the adsorbent's adsorption capacity, which can be applied to the study of the kinetic behavior over the experimental time, and without presenting restrictions on the time of the adsorbent balance. Therefore, the main parameters in relation to the study of the kinetic model of adsorption for Pb^{2+} were calculated and presented for the pseudo-second order model (Table 1).

The pseudo-second order model adapted satisfactorily with the evaluated system considering all studied pH values, with determination coefficient (R^2) ≥ 0.9866 and adjusted coefficient of determination (adj-R^2) ≥ 0.9847 (Table 1). However, only values of R^2 are not correct indicatives of the adjustment of experimental data with the kinetic model, but only when the experimental data are in agreement with calculated data by the model. Note that the data presented in Table 1 indicate that the values of q_e (calculated) are close to those values of the q_{exp} (experimental) for pseudo-second order model. In general, pH 6 was the one that presented the best adsorption constants as a function of time for the pseudo-second order model. Thus, for future studies, this pH will be considered to ensure that the only speciation for lead solution is Pb^{2+} (Figure 5), in addition to presenting conditions for evaluation systems closer to the pH found for environmental conditions, for example, in a river, lake, and soil waters used in agricultural practices.

Ca^{2+}

The effect of pH as a function of contact time for the interaction/release of Ca^{2+} in BC evidenced a greater release of the nutrient in an acidic medium (pH 4 and 6), with pH 4 having the highest release of the nutrient for all evaluated systems (Figure 7).

The release of Ca^{2+} present in the BC is an indicative of the potential use of the BC of biomass origin in agricultural sectors. Thus, it was necessary to study the release mechanisms of this nutrient present in BC and its structural dynamics to enable the possibility of application in agricultural systems in the form of organometal fertilizers.

The Ca^{2+} release capacity was fast, occurring mainly in the first 60 min, with pH 4 being more favorable for the release of the nutrient. The-release capacity of the nutrient for BC1, BC2, BC3 and BC4 was 0.686; 0.700; 0.765 and 0.655 mg g^{-1}, respectively.

In terms of agricultural application, for a production of 25 tons of roots and aerial part of cassava *per* hectare, 46 kg of Ca^{2+} are needed, and the cassava culture adapts to soils with low fertility, as it has the capacity to respond positively to the application of fertilizers and to export large amounts of nutrients from the soil.[54] In this context, the

Table 1. Relationship of pseudo-second order kinetic parameters in the adsorption of Pb^{2+} in BC produced under different conditions of pyrolysis temperature as a function of pH variation

Material	pH	q_{exp} / (mg g^{-1})	Pseudo-second order			
			q_e / (mg g^{-1})	k_2 / (mg g^{-1} min^{-1})	R^2	Adj-R^2
BC1	4.0	2.36	2.33	0.0426	0.9997	0.9996
	6.0	2.36	2.25	0.0728	0.9991	0.9989
	8.0	2.16	2.08	0.0138	0.9866	0.9847
BC2	4.0	2.37	2.29	0.1978	0.9995	0.9994
	6.0	2.20	2.12	0.0753	0.9997	0.9996
	8.0	2.14	2.06	0.1176	0.9999	0.9999
BC3	4.0	2.19	2.15	0.0510	0.9997	0.9997
	6.0	2.34	2.25	0.0220	0.9958	0.9952
	8.0	2.03	1.96	0.1050	0.9994	0.9993
BC4	4.0	2.21	2.13	0.0420	0.9990	0.9989
	6.0	2.07	2.07	0.0550	0.9998	0.9997
	8.0	2.31	2.06	0.0208	0.9985	0.9983

q_{exp}: experimental adsorbed amount; q_e: amount adsorbed obtained for the biochar (BC) using the pseudo-second order model; k_2: values of the constant for the reaction; R^2: determination coefficient; Adj-R^2: adjusted coefficient of determination. BC1, 350 °C; BC2, 450 °C; BC3, 500 °C; BC4, 550 °C.

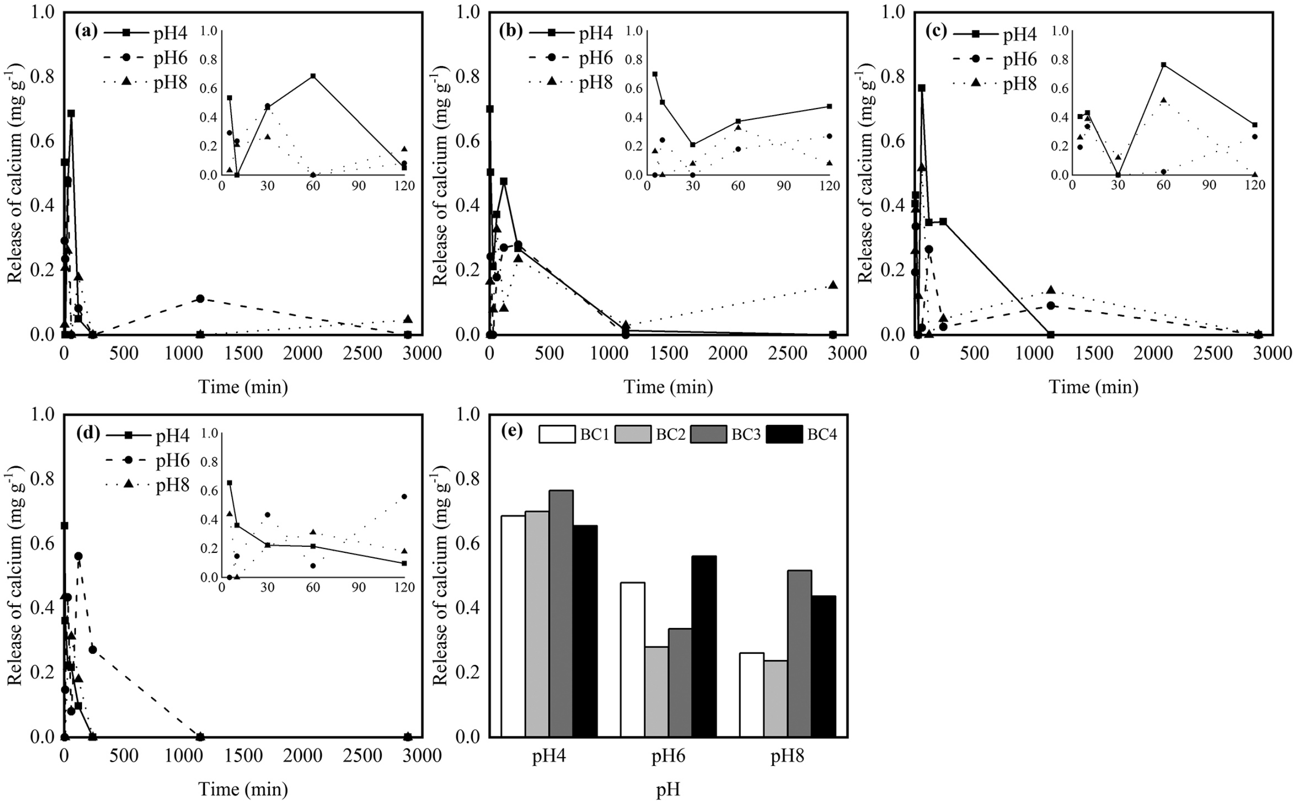

Figure 7. Influence of pH and time on the BC calcium release process: (a) BC1; (b) BC2; (c) BC3; (d) BC4; and (e) Ca^{2+} release capacity produced under different pyrolysis temperature conditions: BC1, 350 °C; BC2, 450 °C; BC3, 500 °C; and BC4, 550 °C. The inserts in (a), (b), (c), and (d) represent values in an increased scale (time from 0 to 120 min) for better visualization.

results of this research demonstrate that the application of BC has the potential to result in a release of nutrient Ca^{2+} of approximately 13.1 to 15.3 kg ha^{-1} in soil, considering an application of 20 t ha^{-1} of the BC of CW. These values correspond from 28.48 to 33.26% of the total Ca^{2+} required for the production of cassava.

The Ca^{2+} release by BC produced by CW biomass shows the potential of BC to act in improving soil fertility and in reducing costs and environmental impacts through the application of fertilizers. Also, it provides benefits to the soil, to the microorganisms present in the soil, and to the environment, contributing to agricultural productivity through the use of residues in the planting and cultivation of cassava.

Contents of nutrients and contaminants

The concentrations of nutrients and contaminants determined in the raw material and in the BC show that, in general, the elements Al, Ba, Mn, Sr, and Zn are in higher concentrations in all samples. The nutrients Co and Mo were below the limit of quantification (< LOQ) in CW and BC, while the contaminants Cd and Cr were < LOQ only in fresh material (CW), being quantified in BC. This can be attributed to the increase in the concentration of metallic species by the process of decomposition of plant material during pyrolysis, causing the loss of many chemical species of CW in the form of gas and, consequently, increasing the concentration of metallic species in the solid phase of BC by the loss of mass of the raw material (Table 2).

The limits of detection (LOD) and quantification (LOQ)[55,56] and the emission wavelengths of each element are described in Table 3.

The values obtained for Ba, Cd, Cr, Cu, Ni, Pb, Mn, and Zn were lower than those established by the National Environmental Council (CONAMA, resolution No. 420/2009),[57] which establishes prevention values for soil quality in terms of the present chemical species and establishes guidelines for environmental management. Besides, the amount of nutrients is also one of the very important properties in the composition of BC, as they are necessary elements for plant growth. In this sense, metals such as Zn, Cu, and Mn, when in adequate concentrations, are important for plants, being considered essential micronutrients.[58]

Thus, BC produced from CW waste can be a viable strategy to enhance agricultural production as a soil

Table 2. Concentrations of the metallic species Al, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sr, and Zn associated with fresh samples (CW) and biochar (BC), determined by MP-AES (n = 3)

Metal	CW / (mg g^{-1})	BC1 / (mg g^{-1})	BC2 / (mg g^{-1})	BC3 / (mg g^{-1})	BC4 / (mg g^{-1})
Al	280.65 ± 17.09	1495.25 ± 51.37	3116.33 ± 168.36	2598.38 ± 58.87	2571.33 ± 17.13
Ba	5.04 ± 0.18	12.14 ± 0.65	11.69 ± 0.35	11.15 ± 0.18	11.78 ± 1.15
Cd	< LOQ	0.03 ± 0.00	0.04 ± 0.00	0.08 ± 0.00	0.06 ± 0.00
Co	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Cr	< LOQ	2.33 ± 0.07	2.99 ± 0.09	3.29 ± 0.01	3.53 ± 0.13
Cu	1.61 ± 0.10	5.63 ± 0.29	6.34 ± 0.14	6.85 ± 0.05	6.38 ± 0.05
Mn	4.06 ± 0.20	12.10 ± 0.65	13.09 ± 0.36	14.39 ± 0.29	17.53 ± 0.78
Mo	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Ni	3.22 ± 0.53	15.68 ± 0.82	7.13 ± 1.13	11.61 ± 1.03	8.23 ± 0.66
Pb	1.35 ± 0.00	5.78 ± 0.07	5.11 ± 0.26	4.64 ± 0.03	4.68 ± 0.09
Sr	16.74 ± 0.57	36.98 ± 1.87	37.53 ± 0.96	38.93 ± 0.65	37.93 ± 4.96
Zn	9.53 ± 0.73	29.03 ± 1.41	31.36 ± 1.93	30.01 ± 0.65	28.98 ± 0.07

CW: cassava waste; BC: biochar (BC1, 350 °C; BC2, 450 °C; BC3, 500 °C; BC, 550 °C); < LOQ: below the limit of quantification.

Table 3. Wavelength of the elements analyzed by MP-AES, and their limits of detection (LOD) and quantification (LOQ)

Element	Wavelength / nm	LOD / (mg L^{-1})	LOQ / (mg L^{-1})
Al	396.152	1.15×10^{-1}	3.50×10^{-1}
Ba	455.403	1.00×10^{-4}	4.00×10^{-4}
Cd	228.802	1.50×10^{-3}	4.50×10^{-3}
Co	340.512	4.40×10^{-3}	1.34×10^{-2}
Cr	425.433	4.70×10^{-3}	1.41×10^{-2}
Cu	324.395	1.50×10^{-3}	4.50×10^{-3}
Mn	403.076	1.50×10^{-3}	4.50×10^{-3}
Mo	379.825	4.30×10^{-3}	1.30×10^{-2}
Ni	352.454	3.80×10^{-3}	1.14×10^{-2}
Pb	405.781	2.80×10^{-3}	8.40×10^{-3}
Sr	407.771	6.80×10^{-3}	2.07×10^{-2}
Zn	213.857	6.81×10^{-2}	2.06×10^{-1}

LOD: limit of detection; LOQ: limit of quantification.

conditioner, improving fertility and contributing to the production of food and the quality of life of the population.

Conclusions

The production and characterization of biochar produced from cassava waste showed that the increase in pyrolysis temperature enabled distinct and important characteristics for biochar, such as increased pH and reduced yield. In addition, biochar demonstrated a Pb^{2+} adsorbed amount of 2.03 to 2.37 mg g^{-1} and a Ca^{2+} release capacity of 0.655 to 0.765 mg g^{-1} considering all evaluated systems. In this way, biochar produced from cassava peel residues can be a viable strategy to increase agricultural production and reduce environmental contaminants in areas such as the semiarid region of Brazil.

Acknowledgments

The authors gratefully acknowledge the Federal University of Alagoas for the opportunity to carry out this research. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil (CAPES), finance code 001. This work was financially supported by CAPES, through Pro-equipment Project (proposal No. 189683), No. 11/2014.

Author Contributions

Ricardo R. da Silva performed investigation and writing the original draft; Luciana C. de Oliveira and Gabriele V. M. Gabriel were involved in investigation, review and editing; João I. Soletti and Simoni M. P. Meneghetti were involved in visualization, contributed to equipment acquisition; Mozart D. Bispo, Sivaldo S. Paulino and Geovânia C. de Assis were involved in investigation; Andrea P. Fernandes was involved in visualization and review; Wander G. Botero contributed to supervision, review, editing and funding acquisition.

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Submitted: February 4, 2022