

Biochar and conventional compost reduce hysteresis and increase phosphorus desorbability in iron mining waste

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ABSTRACT: Phosphorus (P) fixation in the soil reduces the utilization of this element by plants and can be one of the main problems for fertilization management in soils containing Fe oxides. As a strategy to minimize the effects of P retention, organic materials, such as biochar or commercial composts, may be useful tools to maintain P availability and delay immobilization of this element in the soil, thereby benefiting, for example, the rehabilitation of areas impacted by Fe mining. The objective of this study was to evaluate the kinetics of P sorption and desorption and the hysteresis index in red mining waste from Fe mining subjected to açai biochar and commercial compost amendments. Therefore, a substrate collected from Fe mining waste piles in the Carajás Mineral Province was incubated for 30 days with açai biochar, commercial compost, and açai biochar + commercial compost at a ratio of 90 % mining waste and 10 % organic amendment (w/w). The P sorption and desorption kinetics were evaluated in a solution containing 10 mg L⁻¹ P at times from 0.5 to 48 h; the data were modeled according to a pseudo-first-order equation considering two types of reaction sites, and the hysteresis index was obtained by the difference between the sorption and desorption isotherms. Treatment of the mining substrate with açai biochar reduced P sorption, while P desorption was increased by up to 60 % by applying biochar and/or commercial compost. Açai biochar also reduced the hysteresis of P sorption from 78 to 54.8 %, in addition to slowing P fixation in this substrate. Thus, this study showed that açai biochar and commercial compost may maximize the benefits of phosphate fertilization during the rehabilitation of areas impacted by Fe mining. However, as these composts can cause different effects on P dynamics in mining waste, their effects on other elements, such as micronutrients, whose availability may be affected, are important to be evaluated.

Keywords: P kinetic, soil recovery, Carajás, organic amendments.

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INTRODUCTION

The extraction of iron (Fe) ore has great socioeconomic importance; however, large amounts of waste are generated annually, and drastic changes in landscape occur through the formation of mining pits and waste piles (Thistle and Langston, 2016). Rehabilitation of these areas requires complex revegetation planning and soil quality monitoring, which may involve the use of tolerant plants and soil fertility management (Bateman et al., 2019). The low availability of phosphorus (P) is one of the main problems in Fe-rich areas due to the high interaction (in sorption reactions) between P and Fe chemical species (Jiao et al., 2018), which encourages circumventing the difficulties involved in phosphate fertilization management, especially in mining areas where P fertilization is essential to assist the growth of plants in revegetation.

Sorption is the term used to describe the three possible forms of retention of a chemical element or molecule that can occur as adsorption, precipitation, or diffusion, which are processes challenging to differentiate in most experiments (Sparks, 2003). The different forms of P retention are governed by the presence of Fe and Al oxyhydroxides, by the presence and type of silicate minerals, and by specific soil properties such as pH and soil organic matter (OM) content and type (Nobile et al., 2020). The distribution of these factors in the soil controls the availability of P as well as the speed of retention and the reversibility of fixation reactions (Audette et al., 2016). These processes are normally investigated through kinetic experiments.

A kinetic study of P sorption allows a detailed evaluation of the retention dynamics of this element, considering sorption and desorption rates in models, which may involve the presence of fast or slow sorption sites (Aharoni and Sparks, 1991). Sorption and desorption reactions can also be described by isotherms as a function of time, and when sorption and desorption isotherms do not coincide, the irreversibility of the process for that evaluation time becomes evident (hysteresis) (Mosquera-Vivas et al., 2018).

Biochar is produced from anaerobic combustion of organic wastes, sometimes without proper disposal destination, and this is a more recalcitrant material with significant amounts of nutrients in surface and high nutrient retention capacity, but it can also be used as a source of nutrients for the soil (Zhang and Ok, 2014). Such material is effective for contaminant retention in the soil, in addition to pollutant control in waters (Yin et al., 2017).

Organic matter can be a crucial factor to increase the recovery of previously adsorbed P (Guedes et al., 2016) and the application of organic compost and biochar may increase P availability in the soil (Wei et al., 2015; Zhou et al., 2020). However, in areas of Fe mining that are rich in iron oxides and hydroxides and where revegetation and environmental rehabilitation are challenging (Gastauer et al., 2018), few studies have examined how these amendments can change the retention rate and the reversibility of the process and contribute to greater P availability for plant growth in mined areas under rehabilitation.

Rehabilitation of mined lands is challenging due to the lack of nutrients and OM in mined substrates. In Fe mining areas that are in an advanced recovery stage, P lability and availability are high. However, in areas that are in an early recovery stage, the efficiency of phosphate fertilization is low (Guedes et al., 2020), thus creating a need to develop a strategy to maintain the availability of P for a longer time; such a strategy is especially needed in the initial stages of plant development, which is fundamental to the success of soil recovery practices and the establishment of permanent vegetation.

Therefore, in areas of Fe mining, the application of organic amendments may be an efficient method to maintain P availability for longer periods and prevent its loss due to sorption, which may increase the efficiency of phosphate fertilization in these areas. Our hypothesis is that the application of açai biochar and compost prolongs the availability of P and increases the reversibility of its sorption in an Fe mining substrate. The objective

of this study is to evaluate P sorption and desorption kinetics and the hysteresis index in Fe mining tailings treated with açai biochar and organic compost.

MATERIALS AND METHODS

Substrate origin

The substrate used in this study was red mining waste derived from iron ore exploration in one of the largest mining complexes in the world, in Carajás Mineral Province, Brazil (6° 3' 15.42" S and 50° 10' 43.52" W). These red mining wastes are deposited in specific areas, forming waste piles, which are revegetated to trigger their environmental rehabilitation. An overview and the specific location where the substrate was sampled are shown in figure 1.

Application of treatments

The experiment was conducted under controlled temperature and humidity conditions in a greenhouse environment using 2-dm³ pots. The treatments were applied on a dry matter basis (w/w). Due to low OM content, the treatments were applied in a proportion of 10 %. Thus, the following amounts were applied: 90 % mining waste with 10 % açai biochar (WB); 90 % mining waste with 10 % compost (WC); 90 % mining waste with 5 % of each amendment (açai biochar and compost - WBC); and mining waste without the addition of any organic compost (control treatment, W). Each treatment had three replicates. After the mixtures were generated, the samples were incubated at approximately 60 % of the field capacity moisture for 30 days for subsequent evaluation. The samples were fully stirred for 10 min daily to ensure homogeneous distribution of treatments.

Production and characterization of biochar and organic compost

Açai biochar was produced from açai seeds (*Euterpe oleracea*) acquired from urban markets in the city of Belém, Pará. Açai seeds are consumed in such large quantities in Amazonian regions that açai application for soil enhancements (rehabilitation and further applications) can be a viable solution to manage its residues (Sato et al., 2019). The material was washed and then dried in an oven at 50 °C for 24 h. The pyrolysis temperature was 400 °C for 4 h in a muffle furnace (Quimis, model Q318M24) with a

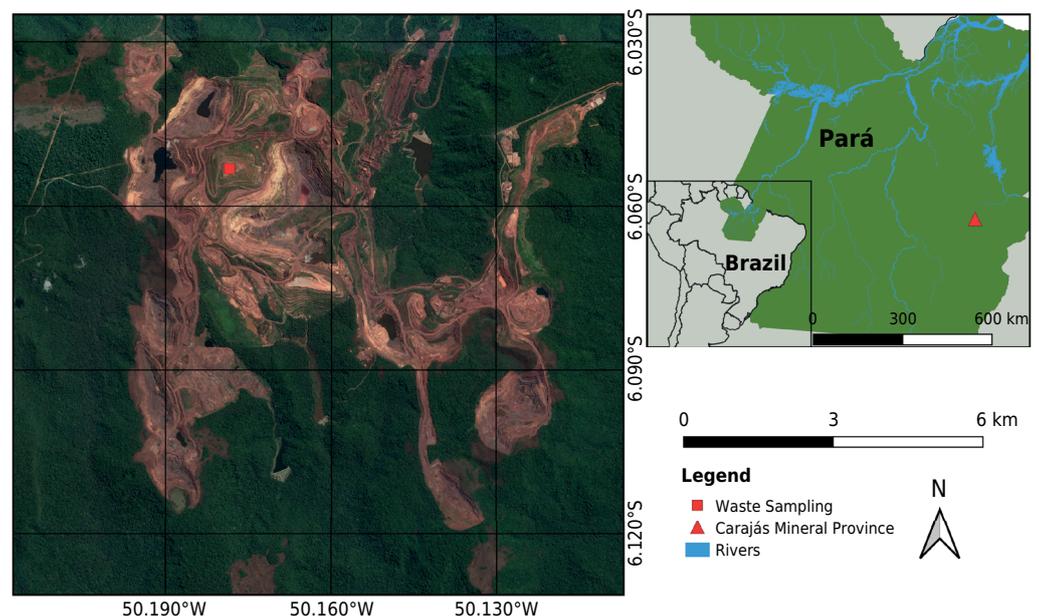


Figure 1. Location of the iron mine and waste sampling area.

heating rate of $3.3\text{ }^{\circ}\text{C min}^{-1}$, maintaining the final temperature for 1 h to slow pyrolysis. The material was kept inside the muffle furnace to cool slowly for subsequent weighing. After pyrolysis, the biochar was macerated in a porcelain crucible and passed through a 2-mm sieve. Organic compost is routinely applied in Fe areas under rehabilitation in Carajás. This material was purchased and resulted from the composting of plant waste from different species with a sandy loam soil at ratios kept confidential according to the mining company's asset security policy.

Macro- and micronutrient contents in the açai biochar and compost were analysed using the Environmental Protection Agency (EPA) 3050b method. For extraction, the samples were added to microwave-transparent vessels containing 10 mL nitric acid, heated to $95\text{ }^{\circ}\text{C}$, and refluxed for 15 min; then, samples were cooled before the addition of 5 mL concentrated HNO_3 , heated to $95\text{ }^{\circ}\text{C}$, and refluxed for 30 min. The elements were quantified by inductively coupled plasma mass spectrometry (ICP-MS). The pH was evaluated in water with a ratio of 1:5 (Singh et al., 2010). The cation exchange capacity (CEC) was measured by extraction with ammonium acetate ($\text{NH}_4\text{CH}_3\text{CO}_2$) (Song and Guo, 2012). Briefly, 40 mL of 1 mol L^{-1} of ammonium acetate was added to 0.1 g of biochar or compost (1 g in the case of soil) in a 50-mL tube and subsequently stirred (20 min) and filtered. Next, the residue was washed with 30 mL of isopropanol (to remove the excess NH_4) and 40 mL of $\text{KCl } 1\text{ mol L}^{-1}$ (to remove NH_4 from soil charges). The NH_4^+ contained in the KCl solution was quantified using the salicylate colorimetric method (Hagemann et al., 2017), and the CEC ($\text{cmol}_c\text{ kg}^{-1}$) was calculated by normalizing the amount of NH_4^+ with the biochar or compost weight (0.1 g). The characterization of compost and biochar is presented in table 1.

Chemical analysis of the mining waste after incubation

Preparation of the samples for chemical analysis included air drying and sieving using 2-mm sieves. The analyses were performed according to Teixeira et al. (2017): pH was determined in water and $\text{KCl } 0.1\text{ mol L}^{-1}$ (1:2.5 soil:solution); K and available P were extracted with Mehlich-1 solution (Mehlich, 1953), where K was determined by flame photometry and P was determined by colorimetry; Ca^{2+} , Mg^{2+} , and Al^{3+} were extracted with $\text{KCl } 1\text{ mol L}^{-1}$; Ca^{2+} and Mg^{2+} were determined by atomic absorption spectrometry and Al^{3+} by titration; and potential acidity (H+Al) was determined via extraction with 0.5 mol L^{-1} of calcium acetate and quantified by titration. The available Fe, Cu, Zn, and

Table 1. Chemical characterization of organic compost and biochar

Properties	Biochar	Compost
pH(H_2O)	6.7 ± 0.2	7.2 ± 0.2
N (%)	2.2 ± 0.1	0.91 ± 0.1
Na (%)	$0.02\leq 0.1$	$0.14\leq 0.1$
K (%)	$0.8\leq 0.1$	$0.12\leq 0.1$
S (%)	$0.08\leq 0.1$	$0.21\leq 0.1$
Ca (%)	$0.1\leq 0.1$	4.34 ± 0.8
Mg (%)	$0.11\leq 0.1$	$0.28\leq 0.1$
C (%)	72.2 ± 12.3	25.32 ± 5.2
P (mg dm^{-3})	2910 ± 58.1	1660 ± 47.2
B (mg dm^{-3})	10.0 ± 1.9	20.0 ± 2.6
Cu (mg dm^{-3})	20.9 ± 1.9	27.4 ± 2.7
Fe (mg dm^{-3})	$0.03\leq 0.1$	3.65 ± 0.8
Mn (mg dm^{-3})	524 ± 22.3	1320 ± 12.2
Zn (mg dm^{-3})	32 ± 7.2	52 ± 4.4
CEC ($\text{cmol}_c\text{ dm}^{-3}$) ⁽¹⁾	785.6 ± 29.4	1159.1 ± 19.5

⁽¹⁾ CEC: cation exchange capacity at pH 7. Mean \pm standard deviation (SD) of the mean of three replicates. Within rows, means followed by the same letter do not differ by Tukey's test ($p<0.05$).

Mn contents were extracted with diethylenetriaminepentaacetic acid (DTPA) solution at pH 7.3 and determined by atomic absorption spectrometry, and B was extracted with hot BaCl₂ (Camargo et al., 2009). Total N was extracted by the Kjeldahl method, and S-SO₄⁻² was extracted with Ca(H₂PO₄)₂.H₂O solution in 2 mol L⁻¹ of acetic acid containing 500 mg kg⁻¹ of P and determined by turbidimetry (Camargo et al., 2009). The CEC was analyzed according to Song and Guo (2012). The OM content was estimated by the soil organic carbon content determined by wet combustion (Teixeira et al., 2017).

Sorption and desorption experiments

The maximum P sorption capacity was evaluated by the batch method according to Graetz and Nair (2009). It was used 1 g of air-dried incubated substrates (<2 mm), 25 mL of solutions containing P at different concentrations of 0, 40, 80, 120, and 240 mg L⁻¹ in the form of KH₂PO₄ was added using an ionic strength of KCl 0.01 mol L⁻¹ at pH 6.4. The doses of P were estimated according to P remaining (Alvarez V et al., 2000). All samples were stirred for 24 h at a temperature between 24 and 25 °C, centrifuged at 4000 rpm for 10 min, and then filtered through Whatman 42 filter paper. The P concentration in the supernatant was analyzed by colorimetry according to Murphy and Riley (1962). The maximum P sorption capacity was determined by the hyperbolic shape of the Langmuir model according to equation 1, and its parameters were obtained by linearization of the hyperbolic model.

$$x/m = K_L C \beta_L / 1 + K_L C \quad \text{Eq. 1}$$

in which x/m is the amount of P sorbed in mg g⁻¹, K_L is the Langmuir constant relating to bond energy in L mg⁻¹, C is the concentration of P in the equilibrium solution in mg L⁻¹, and β_L is the maximum P sorption capacity in mg kg⁻¹.

To evaluate the P sorption and desorption kinetics, 25 mL of a solution containing 10 mg L⁻¹ of P in the form of KH₂PO₄ at an ionic strength of KCl 0.01 mol L⁻¹ was added to 1 g of dry soil and stirred for 0.5, 1, 1.5, 2, 3, 4, 5, 6, 12, 24, and 48 h. Next, each sample was centrifuged and filtered. Then, the samples were washed with 25 mL of distilled water with stirring for 5 min, centrifuged, and then filtered as described above. Desorption was evaluated using only KCl 0.01 mol L⁻¹ immediately after washing, considering its corresponding sorption time in each sample.

Modeling of kinetics data

The P sorption and desorption kinetics were described using a pseudo-first-order equation considering the presence of two types of reaction sites (Aharoni and Sparks, 1991) as described by Guedes et al. (2016) according to equations 2 and 3.

$$dq/dt = k_1 (Fq_{max} - q) \quad \text{for } q < qF \quad \text{Eq. 2}$$

$$dq/dt = k_2 [(1 - F)q_{max} - q] \quad \text{for } q \geq qF \quad \text{Eq. 3}$$

in which dq/dt is the sorption and desorption rate in mg kg⁻¹ h⁻¹; k_1 is the sorption or desorption rate constant for fast sites (h⁻¹); k_2 is the sorption or desorption rate constant for slow sites (h⁻¹); F is the fraction of fast sites; q_{max} is the maximum sorption or desorption under the evaluated experimental conditions (mg kg⁻¹); q is the concentration of sorbed or desorbed P; and qF is the concentration of sorbed or desorbed P at the moment of transition from fast sites to slow sites obtained by two lines fitted to q vs. dq/dt , where qF corresponds to the intersection. The value of F is calculated as qF/q_{max} . If only one type of site is present, $F = 1$, and the model coincides with equation 2 (Pérez-Novo et al., 2011).

The hysteresis index (H) was calculated according to the principle proposed by Deng et al. (2010) and adapted by Guedes et al. (2016) based on the difference between areas under the sorption and desorption isotherms according to equation 4.

$$H = \left(\frac{A_s - A_d}{A_s} \right) \times 100 \% \quad \text{Eq. 4}$$

in which A_s is the area under the sorption isotherm (mg h kg^{-1}) for t ranging from 0 to 24, and A_d is the area under the desorption isotherm at the same time variation (mg h kg^{-1}).

Statistical analysis

All analyses were performed in triplicate, and the data were statistically processed in the R environment v3.5.3 (R Development Core Team, 2018). Descriptive statistics and analysis of variance (ANOVA) were performed, and when significant differences were observed, the least significant difference (LSD) post hoc test was applied. Pearson's correlation analysis was also performed to determine correlations between the sorption data and the characteristics of the substrates.

RESULTS

Soil condition and nutrient availability

The mixtures of mining waste with compost (WC), biochar (WB), and both biochar and compost (WBC) increased the pH and CEC of the tailings, while the addition of both organic treatments (singly or combined) increased the OM content, with the highest value obtained by the addition of compost (Table 2).

The contents of N, P, and K increased in all treatments compared to the control (W), especially with the application of biochar (WB) (Table 2), which is compatible with the amounts of N, P, and K observed in the biochar (Table 1). Furthermore, the contents of Na, S, Ca, Cu, and Fe were higher in WC, and the application of biochar caused reductions

Table 2. Changes in soil properties in mining waste (W) by the addition of biochar (WB), compost (WC), and a combination of both (WBC)

Property	W	WC	WB	WBC
pH(H ₂ O)	6.4±0.3c	7.4±0.1a	6.9±0.2b	7.4±0.1a
Total N (%)	0.05±0.1d	0.11±0.1c	0.27±0.1a	0.22±0.1b
P (mg dm ⁻³)	22.5±3.1d	49.3±2.3c	62.3±2.1a	58.5±1.9b
Na (mg dm ⁻³)	32.6±2.9c	281.8±13.6a	25.1±3.1d	103.4±16.8b
K (mg dm ⁻³)	57.2±5.1d	138.9±8.9c	335.7±10.4a	277.6±9.8b
S (mg dm ⁻³)	30.0±6.9c	126.7±6.5a	25.6±2.9c	66.4±4.2b
Ca ²⁺ (cmol _c dm ⁻³)	2.3±0.6c	8.7±1.2a	2.3±0.5c	6.6±1.1b
Mg ²⁺ (cmol _c dm ⁻³)	3.3±0.1a	2.9±0.1b	2.8±0.1b	2.8±0.2b
OM (dag kg ⁻¹)	0.5±0.2c	1.7±0.2a	1.0±0.3b	1.2±0.3b
B (mg dm ⁻³)	0.53±0.1a	0.58±0.1a	0.32±0.1c	0.42±0.1b
Cu (mg dm ⁻³)	0.70±0.1c	0.90±0.1a	0.70±0.1c	0.80±0.1b
Fe (mg dm ⁻³)	11.06±1.4c	48.20±4.3a	7.11±1.1d	30.05±2.9b
Mn (mg dm ⁻³)	13.50±2.9c	12.30±3.2c	37.10±1.5a	18.3±2.1b
Zn (mg dm ⁻³)	8.60±0.5a	2.50±0.3b	2.20±0.4b	1.60±0.2c
CEC (cmol _c dm ⁻³) ⁽¹⁾	51.5±3.7b	86.4±2.4a	84.2±2.3a	84.2±2.4a
V% (%) ⁽²⁾	76.4±2.0c	89.8±1.5a	83.6±1.2b	89.8±1.7a
Clay (g kg ⁻¹)	270	272	272	272
Silt (g kg ⁻¹)	125	124	124	125
Sand (g kg ⁻¹)	605	604	604	603

⁽¹⁾ CEC: cation exchange capacity at pH 7; ⁽²⁾ V%: bases saturation. Mean±standard deviation (SD) of the mean of three replicates. Within rows, means followed by the same letter do not differ by Tukey's test ($p < 0.05$).

in the availability of these elements, including the Mg content, while the application of both biochar and compost (WBC) resulted in intermediate values (Table 2).

Cumulative sorption and desorption and the hysteresis index

The WB treatment reduced the sorption of P (Figure 2), which reached a maximum value of 103.4 mg kg⁻¹ (Table 3) that was lower than those for all other treatments. However, all treatments with the addition of organic amendments increased the desorption of P (Figure 3), recovering up to 60 % more retained P than that in the mining waste without the addition of biochar and/or compost. In this context, high correlations were observed between Q_{max} of P desorption and some soil properties such as pH and OM.

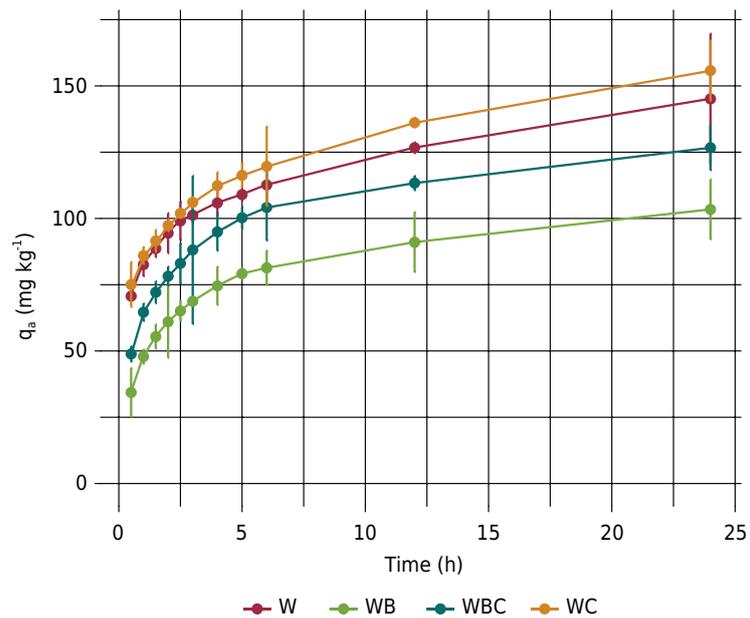


Figure 2. Cumulative P sorption (q_a) as a function of contact time in Fe mining waste (W) enriched with organic compost (WC), biochar (WB), and a combination of both amendments (WBC).

Table 3. Kinetic parameters of P sorption by the pseudo-first-order model and hysteresis indices for sorption in Fe mining waste (W) enriched with organic compost (WC), biochar (WB), and a combination of both amendments (WBC)

Treatment	$qF^{(1)}$ mg kg ⁻¹	$F^{(2)}$ -	$Q_{max}^{(3)}$ mg kg ⁻¹	$k1^{(4)}$ h ⁻¹	$k2^{(5)}$ h ⁻¹	$H^{(6)}$ %
Sorption						
W	88.6b	0.61a	145.1b	8.11	0.04	-
WC	91.5a	0.59b	155.7a	9.42	0.04	-
WB	55.4d	0.54d	103.4d	3.14	0.59	-
WBC	72.1c	0.57c	126.7c	4.17	0.71	-
Desorption						
W	13.6c	0.41a	33.0c	5.76	0.04	78.37a
WC	17.3b	0.34b	51.2a	1.69	0.13	65.20b
WB	14.3c	0.31b	45.6b	6.08	0.08	54.80d
WBC	22.4a	0.45a	49.3a	2.38	0.13	59.87c

⁽¹⁾ Concentration of P at the moment of transition from fast to slow sorption or desorption sites; ⁽²⁾ Fraction of fast sorption or desorption sites; ⁽³⁾ The maximum amount of sorption or desorption under experimental conditions; ⁽⁴⁾ and ⁽⁵⁾ the constants related to fast sites and slow sites, respectively; ⁽⁶⁾ The hysteresis index (%). Within columns, means followed by the same letter do not differ by Tukey's test ($p < 0.05$).

Waste not treated with organic amendments had a high hysteresis index (Table 3), and more than 78 % of P was sorbed in the non-reversible form. In turn, enrichment of mining waste with açai biochar and compost, either individually or in combination, reduced the hysteresis index of P sorption, favoring recovery of the sorbed P; the application of açai biochar alone was the most efficient (55 %) in reducing this hysteresis.

Sorption and desorption kinetics

A higher sorption rate was initially observed with all treatments than in control, followed by a significant reduction in the sorption rate as a function of cumulative sorption (Figure 4), showing higher F values and indicating a predominantly fast sorption process.

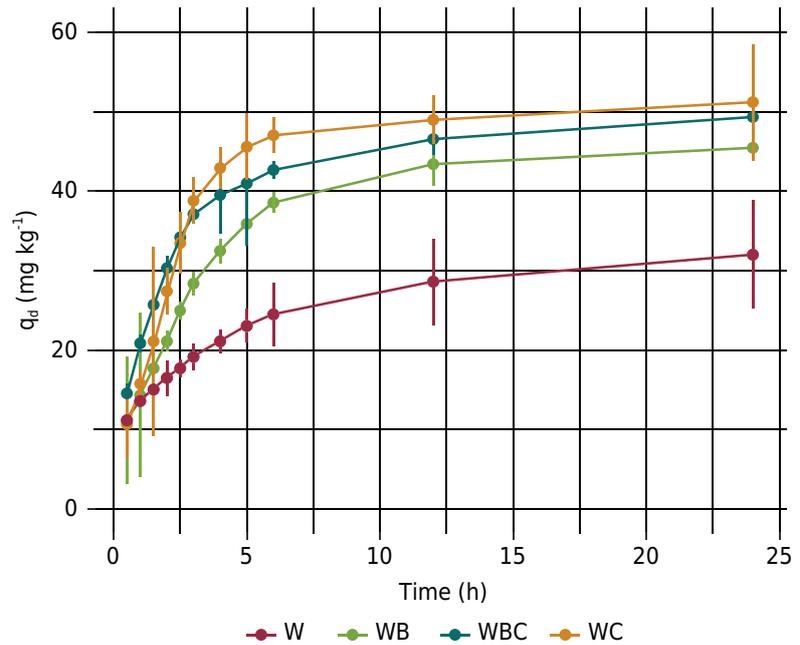


Figure 3. Cumulative P desorption (q_d) as a function of contact time in Fe mining waste (W) enriched with organic compost (WC), biochar (WB), and a combination of both amendments (WBC).

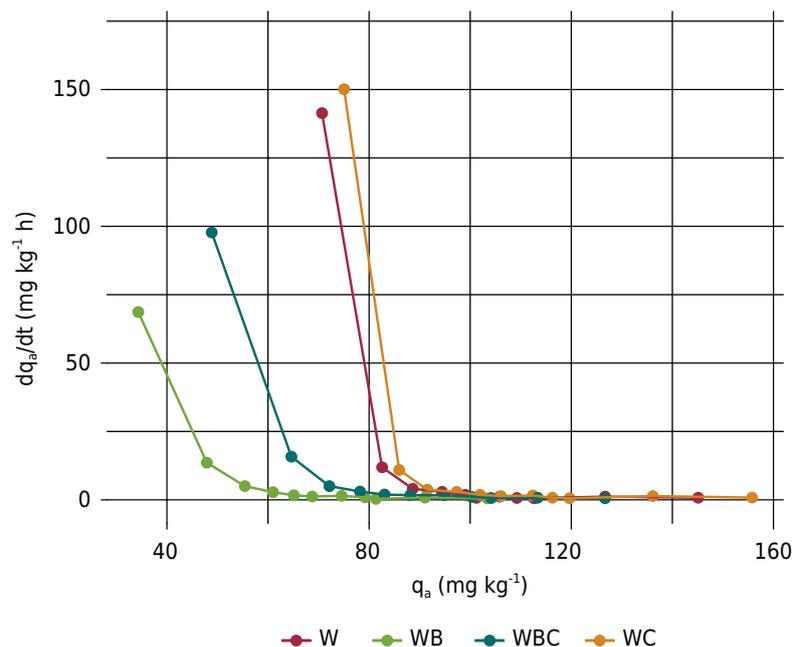


Figure 4. Phosphorus sorption rates in Fe mining waste (W) enriched with organic compost (WC), biochar (WB), and a combination of both amendments (WBC).

Interestingly, this process occurred more slowly when biochar was added to the tailings, where the lowest F values were observed (Table 3). In addition, the P desorption rates were slower in WB and WC, generating lower F values and evidencing processes with a predominance of slow desorption sites (Figure 5).

Maximum sorption capacity

Figure 6 shows the reductions in the maximum P sorption capacity with the application of açai biochar, compost, and the combination of both organic amendments. The WB and WBC treatments reduced the maximum P sorption capacity of mining waste, while WC increased the P sorption capacity, contributing to higher P retention than that in untreated mining waste (W).

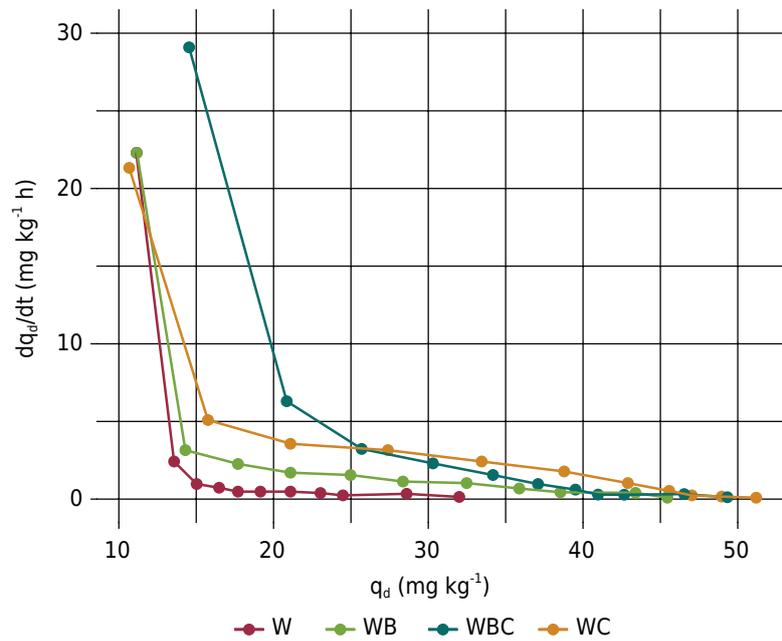


Figure 5. Phosphorus desorption rates in Fe mining waste (W) enriched with organic compost (WC), biochar (WB), and a combination of both amendments (WBC).

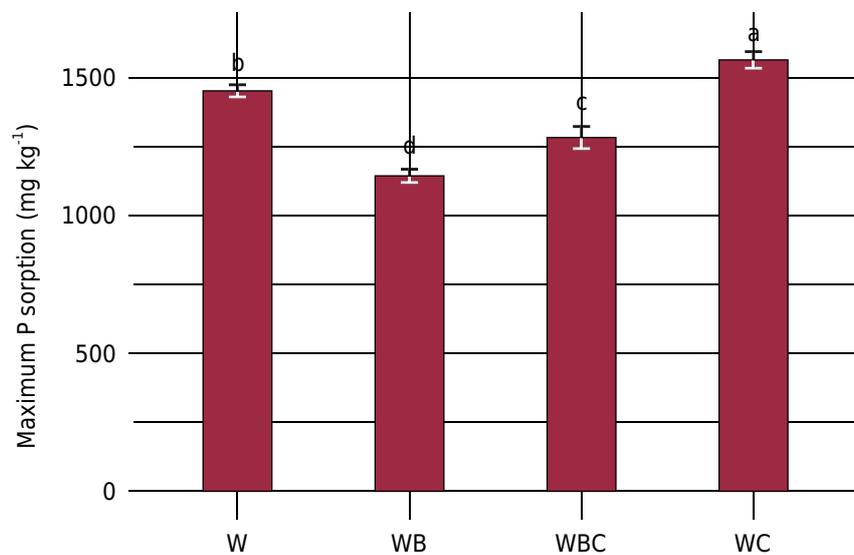


Figure 6. Maximum P sorption capacity in mining waste (W) treated with organic compost (WC) and biochar (WB) alone and in combination (WBC). Means followed by the same letter do not differ by Tukey's test ($p < 0.05$).

DISCUSSION

Influence of organic amendments on the nutrient availability of mining waste

The application of açai biochar and compost had several beneficial effects on the examined mining waste (increasing the soil OM content and CEC and reducing soil acidity). The increase in pH may be associated with the high contents of exchangeable bases present in these materials and with the reduced concentration of exchangeable H^+ due to sorption reactions on the surface of biochar (Tan et al., 2017). Furthermore, the alkalinity of compost and biochar should always be considered a possible soil acidity reducer (Tian et al., 2018). The CEC increases are commonly observed with the addition of various types of organic materials, including biochar, to the soil; these increases occur mainly due to the high amounts of phenolic and carboxylic functional groups in the OM structure, which generate electrostatic attraction forces capable of retaining large amounts of exchangeable bases (Chathurika et al., 2016; Tian et al., 2018).

As detected in this study, another benefit of incorporating biochar or compost was the increased availability of nutrients in incubated mining waste. The OM in biochar can supply part of the nutrients to the soil, which also occurs with composted organic fertilizers (Laird et al., 2010). On the other hand, some micronutrients may have lower availability because the increased pH may decrease the solubility of these elements (Manolikaki and Diamadopoulos, 2020). In addition, it is important to consider a possible effect of biochar on adsorption of cationic micronutrients, which can be improved due to the reduction in soil pH and high electronegativity of these materials (Purakayastha et al., 2019), highlighting the importance of testing the individual influence of each eventual amendment on the target substrate. Similar results were found by Karimi et al. (2020), who reported reductions in micronutrients and pH after the application of 2 % biochar. The increased availability of some nutrients has been reported as one of the main benefits of applying biochar or compost, which is a promising alternative for improving soil fertility management (Ding et al., 2016; Li et al., 2020). In Fe mining areas, the incorporation of this type of organic material may favor rehabilitation of impacted areas, stimulating plant growth and soil cover. However, some studies recommend caution in establishing organic amendments doses, and short-, medium-, and long-term evaluations are necessary due to the use of highly recalcitrant substances such as biochar (Yi et al., 2020; Zhou et al., 2020).

Influence of açai biochar and compost on the sorption and desorption of P

The lower sorption of P onto Fe mining waste treated with biochar may be related to the increase in pH, which favours an increase in P availability due to deprotonation of the OH^- groups on the surfaces of variable charge minerals, such as kaolinite, and Fe oxides present in high amounts in Fe mining areas (Solovitch et al., 2010). In addition, biochar has a high cation retention capacity, which can cause a significant delay in P sorption because the higher number of negative surface charges generates anion repulsion forces (Jiang et al., 2015). The raw material used for biochar production is also one of the factors that can impart a lower P sorption capacity to biochar because, together with the pyrolysis temperature, it determines the formation of surface charges (Vandecasteele et al., 2017). This same type of biochar was evaluated by Dias et al. (2019), who found a lower adsorption capacity than that of biochar produced from materials such as kernel and Brazil nutshells. Another factor related to lower P sorption is the presence of coexisting ions, which reduce P retention through competition (Ngatia et al., 2019). In the present study, this factor was related to the high number of sulfate ions observed in the untreated tailings, which decreased in the presence of biochar.

The application of biochar and compost resulted in higher P desorption than that for the untreated mining waste, which may be related to the lower binding energy for P retention

in the soil with these materials (Han et al., 2018). In addition, biochar and compost are potential sources of P for the soil and can increase the solubility and availability of P by increasing the pH (Ch'ng et al., 2014; Ngatia et al., 2017), which is consistent with the correlations observed between Q_d max and pH. Increased P desorption was also observed by Cui et al. (2011), who analyzed the same phenomenon with ferrihydrite minerals in the presence of biochar, confirming that even under high Fe oxide content conditions, P desorbability is increased in the presence of biochar.

The greater effect of hysteresis observed in the mining waste not treated with organic amendments indicates a high capacity for P retention in a slightly reversible process. In environments with high levels of Fe oxides, the interactions between phosphates and the soil matrix may be predominantly P retention reactions due to the presence of crystalline and amorphous Fe oxides, which favor the formation of bidentate and binucleate bonds in an internal sphere complex, show high binding energy, and hinder P desorption (Barrow et al., 2015).

The application of biochar and compost increased the reversibility of P sorption in Fe mining waste, allowing almost 50 % of the sorbed P to return to the soil solution. According to Hiemstra et al. (2013), organic materials can promote the accumulation of high/low-molecular-weight organic acids responsible for blocking Fe and Al oxide sorption sites, resulting in a smaller P retention force and higher P availability. In addition to competing with the soil mineral phase, biochar can solubilize a large amount of P (Rashmi et al., 2019). A similar trend was observed by DeLuca et al. (2009), who reported that biochar application increased P availability even without the addition of phosphate fertilizers. Likewise, the application of compost may cause a similar effect, possibly due to the release of nutrients, among which P is one of the most abundant nutrients (Ch'ng et al., 2014).

In this study, due to the high affinity between red mining waste and P, the importance of soil conditioners such as biochar and compost for minimizing the impacts of soil P retention is evident. Much of the P is expected to be retained shortly after its application to the tailings. However, the incorporation of biochar and compost can promote greater utilization of P, which is released more slowly, favoring the maintenance of P levels for longer periods, which may increase the likelihood of absorption by plants (Islas-Espinoza et al., 2014; Sun et al., 2018).

Phosphorus kinetics

The sorption and desorption kinetics of P are described at two moments according to the pseudo-first-order model, which considers the presence of two types of sorption and desorption sites. Thus, at the first moment, the process occurs predominantly by fast sites (with high sorption or desorption rates), and at the second moment, a sharp decrease in the sorption or desorption rate occurs, indicating saturation of the fast sites and a predominance of slow sites. In the present study, P sorption was faster in the mining waste without the addition of biochar and compost than in the substrate with the organic products. This result is associated with the presence of difficult-to-access sites and blockage of these sites (Afif et al., 1995). According to Tareq et al. (2019), biochar has microporous structures whose access becomes increasingly difficult as more accessible sites are saturated. In addition, the difficulty of accessing sorption sites also occurs on the surface of Fe oxyhydroxides by means of humic and fulvic acids, which have the ability to temporarily inhibit P sorption, maintaining its availability for a longer time (Fink et al., 2016; Yang et al., 2019). Delayed P sorption was also observed by Matin et al. (2020) when studying different ratios and types of biochar, resulting in an increase in P availability and a reduction in the need for fertilization.

The recovery of sorbed P was also slower after treatment with biochar and organic compost, indicating that these soil conditioners can gradually release P for longer periods.

One possible application of this finding would be using these conditioners to maintain P availability in soils with a high Fe oxide content, which can favor absorption by roots and plant development. The use of organic compost as a source of nutrients has been well studied; however, the application of biochar still requires further investigation due to the ability of biochar to interact with other elements and molecules in the soil. Great potential exists for the use of biochar to maintain the availability of P and other nutrients in the soil (Ding et al., 2016). This potential of biochar was evaluated by Xu et al. (2014), who obtained desorption values of up to 41 % with biochar application. However, the desorption capacity and the desorption rate depend directly on the raw material used for biochar production, the pyrolysis temperature, and the P loading rate (Ding et al., 2016).

Maximum sorption capacity

The reductions in the maximum P sorption capacity promoted by the addition of biochar reinforce the beneficial effect of this material on the maintenance of P availability, even in an environment with a high Fe oxide content. Changes in soil pH, along with the release of organic acids that impede P fixation in the soil, and the competitive effects of other elements in the soil can be considered important factors for the reduction in P sorption (Ngatia et al., 2019). In this context, Nobile et al. (2020) reported that in areas managed with organic composts, P availability depended primarily on changes in pH and the P contents that these materials added to the soil. The benefits of soil conditioning with biochar were evaluated by Matin et al. (2020), who concluded that the use of biochar may increase P availability even after a short application time, reducing the need for fertilization. Therefore, in Fe mining areas, revegetation may benefit from applying these materials to increase the efficiency of phosphate fertilization.

CONCLUSION

This study evaluated the effect of applying açai biochar and organic compost on P sorption and desorption kinetics, as well as its effects on hysteresis, in iron mining waste from the Carajás Mineral Province.

The application of açai biochar was found to reduce P sorption, while the addition of compost and biochar increased the desorption of this nutrient. Both açai biochar and compost promoted a significant reduction in the hysteresis index; however, the largest reduction in this phenomenon occurred with the use of biochar alone. In addition, the application of biochar reduced the sorption rate, generating a delay in P retention and higher P availability for a longer period.

Açai biochar and organic compost may be useful in the rehabilitation of areas impacted by Fe mining as a strategy to maximize the benefits of phosphate fertilization. However, these composts can cause different effects on P dynamics in mining tailings, and it is important to consider their effects on other elements, such as micronutrients, whose availability may be affected.

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SUPPLEMENTARY DATA

Supplementary data to this article can be found online at <https://doi.org/XXX>.

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