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Biochar Chemistry in a Weathered Tropical Soil: Kinetics of Phosphorus Sorption

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Abstract: The phosphorus (P) chemistry of biochar (BC)-amended soils is poorly understood. This statement is based on the lack of published research attempting a comprehensive characterization of biochar's influence on P sorption. Therefore, this study addressed the kinetic limitations of these processes. This was accomplished using a fast pyrolysis biochar made from a mix of waste materials applied to a highly weathered Latossolo Vermelho distrofico (Oxisol) from São Paulo, Brazil. Standard method (batch method) was used. The sorption kinetic studies indicated that P sorption in both cases, soil (S) and soil-biochar (SBC), had a relatively fast initial reaction between 0 to 5 min. This may have happened because adding biochar to the soil decreased P sorption capacity compared to the mineral soil alone. Presumably, this is a result of: (i) Inorganic phosphorus desorbed from biochar was resorbed onto the mineral soil; (ii) charcoal particles physically covered P sorption locations on soil; or (iii) the pH increased when BC was added SBC and the soil surface became more negatively charged, thus increasing anion repulsion and decreasing P sorption.

Keywords: fast pyrolysis; batch method; P retention

1. Introduction

More than 3 billion people live in the tropics, which was larger than the world's population in 1950 [1]. They rely on the soil to provide food, fiber, and bioenergy. Of the 134 million hectares in humid, tropical South America that are potentially arable, 73 million are located in Brazil [1]. The majority of these acres suffers from some level of phosphorus (P) deficiency due to low native soil P content and high P fixation capacity [2]. Therefore, soil P management is fundamental to sustainable agriculture and the health and welfare of millions.

The weathered nature of tropical soils promotes P fixation by Fe and Al oxides which, when chemisorbed to the soil, are not easily released by simple equilibrium desorption [3]. This makes soil P fertilization both inefficient and expensive since large quantities of P are required to overcome the soils' potential to sequester it. The soil management techniques currently used to make fertilizer P more bioavailable either satisfy the P fixation capacity of a soil or prevent soil P fixation. These include applying inorganic P in the planting hole in order to fill the fixation sites in a small soil volume near the roots or using organic matter where the organic matter competition for sorption sites prevents P fixation [4].

These soil management techniques control P sorption and desorption mechanisms while reducing the cost of inputs. Once P enters the soil system it chemically reacts with

the soil surface and eventually reaches an equilibrium or quasi-equilibrium. What happens to P on its way to an equilibrium soil solution concentration is described by the kinetic path of the reaction(s). Likewise, for P on the solid phase to become bioavailable, it must be released from the solid phase while again seeking an equilibrium or quasi-equilibrium with the soil solution. Maybe this state is reached in a system defined by a dynamic biology of microorganisms and plant roots, but certainly it routes toward that state in the kinetic path. The speed kinetics of these reactions that determine the soil solution concentration can affect P bioavailability [5]. However, there are restricted data on the kinetics of these processes in tropical soils which, if more fully understood, could lead to better management of soil solution concentrations.

While a relatively low, but highly buffered, soil P solution concentration is sufficient to meet the needs of many plants, a high soil P fixing capacity combined with fast sorption kinetics and slow desorption kinetics would be an impediment for adequate solution concentrations to be maintained. [5] suggested that soil solution concentrations that provide adequate P bioavailability range from 0.2 to 10 µM, depending on crop type. This conclusion was partially based on work by [6] and [7] who reported adequate concentrations of 0.2 uM for cassava (*Manihot esculenta* Crantz.) to 10 uM for lettuce (*Lactuca* sp.), with intermediate values for peanuts (*Arachis hypogaea* L.), cabbage (*Brassica oleracea*), corn (*Zea Mays*), sorghum (*Sorghum* sp.), soybean (*Glycine max*), and tomato (*Solanum lycopersicum*).

Biochar (BC), a product resulting from the pyrolysis of organic materials, is a soil amendment that affects P bioavailability [8–10]. Under limited circumstances it can be a source of inorganic P [11–13] and it retains nutrients while improving soil physical, chemical, and biological properties [9,14,15].

A key physical feature of most BCs is their highly porous structure and large surface area. This structure can provide refugia for beneficial soil micro-organisms such as mycorrhizae and bacteria, while also influencing the kinetics of the sorption and desorption reactions of important plant nutritive cations and anions. The pore structure should affect the importance of diffusion from the pores to both sorption and desorption reactions. Biochar pyrolysis concentrates nutrients like P, making them more bioavailable and a source for plant uptake [11].

Biochar application to soils affects P complexation with metals (Al^{3+}, Fe^{3+}, and Ca^{2+}), which determine P sorption and desorption reactions [11,16]. Biochar could promote delayed P sorption or precipitation, hence influencing the kinetics of these reactions. Sorption of organic molecules onto BC surfaces reduces the chelation of Al^{3+}, Fe^{3+}, and Ca^{2+} in soil [17] enhancing P desorbability [18] and possibly changing P desorption kinetics. The capacity of BC to influence soil P sorption and desorption kinetics is not well understood, yet the literature suggests a potential influence.

Thereby, agricultural practices have to be applied aimed to decrease phosphorus sorption in tropical soils. Our specific objective in this study was to investigate the role that BC has on the kinetics of P sorption in a soil/BC complex. Our hypotheses were that (1) BC reduces P sorption onto soil due to the covering of potential sorption sites and the role that diffusion may play due to the high porosity of the BC; and (2) during the kinetics of sorption in the presence of BC, the soil solution P concentrations remain higher, which would make P more bioavailable for a longer period of time.

2. Material and Methods

2.1. Biochar Formation and Characterization

The fast pyrolysis BC was developed from a sequence of three distinct BCs produced by sawdust of mixed woods and leaves of elephant grass (*Pennisetum purpureum* Schumach) and sugar cane (*Saccharum officinarum*). The three BCs were combined in a 1:1:1 ratio. Each of these three BCs was the by-product of bio-oil extraction created in a fluidized bed reactor (200 kg h^{-1} capacity) produced by Bioware (Biotechnology company in Campinas, State of São Paulo, Brazil). The procedure was done in a controlled temperature from 450 to 500 °C, under 120 to 250 mm of H_2O pressure for about 8 s in an ambience of 10% air.

The BC's water-soluble nutrients (P, Ca, Mg, K and Na) were determined by sequential water extractions. Twenty grams of the combined BC were mixed through 350 mL of deionized water and shaken for 24 h. The supernatant was filtrated, and the procedure was performed for 30 times. The atomic absorption spectroscopy was used to quantify Ca, Mg, and K in the supernatant. To measure inorganic P, [19] method was used. The dissolved organic carbon (DOC) was measured using a TOC-Analyzer (Shimadzu TOC-VCPH; Columbia MD, USA). Porosity and specific surface area were measured with a Micromeritics ASAP 2021 analyzer sorptometer (Norcross, GA, USA). Microstructure and surface topography was photographed by scanning electron microscopy (515-Philips, Eindhoven, Holland) with a magnification of 42–2000 times and resolution of 3–100 nm (Verhoeven, 1986). The functional groups on the BC surface were analyzed by the method of [20]

According to [21], a few other methods of determining total N [22], pH in water (1:2.5); organic C (volumetric oxidation method), total Ca, Mg, Cu, Fe, Mn, and Zn (extraction by nitric-perchloric acid solution and determined by atomic absorption spectrometry), total K and Na (extraction with nitric-perchloric acid solution and determination by flame photometry), total S (extraction with nitric-perchloric acid solution and determination by photocolorimetry), and the total P (digestion with sulfuric acid and peroxide) were used.

2.2. Soil Collection and Preparation

The study was carried out on a research field in the Fazenda Lageado at the State University of São Paulo in Botucatu, in the state of São Paulo, Brazil (between coordinates: 22°51″ S, 48°26″ W; elevation of 786 m above sea level.). The soil type used was a Latossolo Vermelho distrofico (Brazilian Soil Taxonomic System; or a Typic Kandiudult in the U.S. System or Oxisol for WRB) degraded by laminar erosion of elimination of 20 cm of the surface when the cultivation was started. The climate of the region is classified as type Cwa (Monsoon-influenced humid subtropical climate), according to the Köppen–Geiger's classification, with rainy periods between October and April and dry ones between May and September. The rainfall and temperature averages are 1500 mm/yr and 21.4 °C.

Soil samples were collected at a 30–50-cm depth, air-dried, sieved through a 2 mm screen, and characterized by standard methods (Table 1). The soil surface was removed to avoid contamination from organic matter surface. The chemical properties (Table 1) was determined [23], showing the following: pH in $CaCl_2$ (0.01 M) (1:2.5); total acidity (H + Al) by SMP (Shoemaker-McLean-Pratt) buffer solution (pH 7.0); P, Mg, Ca, and K extraction by "exchangeable ions resin" and quantified by photocolorimetry, K, Ca, and Mg by atomic absorption; exchangeable Al by extraction with 1 M KCl; organic C by the volumetric oxidation method with $K_2Cr_2O_7$ and titration with ammonium ferrous sulphate; B extraction by hot water and determined by photocolorimetry by azometine-H method; Cu, Fe, Mn, and Zn extraction using DTPA (diethylentriaminepentaacetic acid) solution (pH 7.3) and determination by spectrometry of atomic absorption; the potential acidity (H + Al), exchangeable bases, and exchangeable Al were used to calculate the total cation exchange capacity (CEC) and effective cation exchange capacity (CECe).

The samples of the soil were incubated for 240 days under greenhouse conditions. Additionally, completely randomized design was used and designed with three replications of three treatments. The treatments consisted of the following three substrates: Soil alone (S), biochar alone (BC), and soil/BC mixture (SBC) combined (26% by weight or 35% by volume). The biochar used came from a study investigating the formation of biochar soils under long-term occupation of native Amerindians of South America. High levels are found in those soils [24], and have been used in other studies [25–27]. Pots were placed in a greenhouse at an average day temperature of 22 °C, under field capacity of the soil contained in the pots. Samples were air-dried after 240 days in the laboratory and sieved through a 2-mm mesh.

Table 1. Chemical properties of the tropical weathered soil and the fast pyrolysis biochar.

Soil Chemical Properties													
pH	**Ca**	**Mg**	**K**	**Al**	**H+Al**	**CEC**	**P**	**Zn**	**Fe**	**Mn**	**B**	**Cu**	**OM**
CaCl$_2$			mmol$_c$ kg^{-1}						mg kg^{-1}				g kg^{-1}
4.1	3	1	1	11	67	71	6	0.1	58	1	0.1	1	16
Soil/BC Mixture Chemical Properties													
8.0	70	13	41	0	7	132	60	0.8	16	7	5	0.4	27
Fast Biochar Chemical Properties													
N	**P**	**K**	**OM**	**C**	**C/N**	**Ca**	**Mg**	**S**	**Na**	**Cu**	**Fe**	**Mn**	**Zn**
			g kg^{-1}(dry weight)						mg kg^{-1} (dry weight)				
06	1.48	16	550	310	48	21	2	190	580	22	4500	264	42

Source: Morales et al. 2013. [11].

Chemical analysis of the soil and soil/BC mixture (Table 1) was carried out [23] to determine: pH in CaCl$_2$ (0,01 mol L^{-1}) (1:2.5); total acidity (H+Al) by SMP buffer solution (pH 7.0); and P, Mg, Ca, K, and DOC by extraction with exchangeable ions resin then quantified by photocolorimetry. Exchangeable Al was determined by extraction with 1 mol L^{-1} of KCl, while organic C was by the volumetric oxidation method with K$_2$Cr$_2$O$_7$ and titration with ammonium ferrous sulfate. Boron was extracted with hot water and determined by photocolorimetry using the azometine-H method, and Cu, Fe, Mn, and Zn was analyzed with extraction by DTPA solution (pH 7.3) and atomic absorption spectrometry. The cation exchange capacity (CECe) and total cation exchange capacity (CEC) were determined by the extraction of exchangeable bases and exchangeable Al.

2.3. Sorption Studies

The P sorption kinetic study was carried out using two-gram samples of S, SBC, and BC, in triplicate placed in 50-mL centrifuge tubes and gently shaken at 96 cycles min^{-1} for 0.1, 0.2, 0.3, 0.5, 1, 1.5, 2, 3,6, 12, 24, 48, 72, and 96 h with 20 mL of solution containing 400 mg P kg^{-1} of soil. This amount of P is also often found in Terra Preta de Índio [28]. Upon removal from the shaker, the tubes were centrifuged for 10 min at 2000 rpm and the supernatant was removed and filtered through 0.45-µm filter paper. The solution concentration of P in the supernatant was measured colorimetrically [19].

2.4. Statistical Methods

Data were analyzed by fitting sorption curves to each treatment and were regressed against natural logarithms of time to estimate the P sorption (mg kg^{-1}). The linear model as selected for the treatments, and the model coefficients were compared for their equality. To this purpose, we used the likelihood ratio test with accuracy given by the chi-square (χ^2) statistic [29]. This method involves the addition of two independent variables, D1 and D2, in order to calculate the maximum likelihood estimates of the parameters under no restrictions in the parametric space representing the complete model and under restriction in the reduced model. The complete model was adjusted under no restrictions and the reduced model was adjusted with respect to restrictions defined in H$_0$.

3. Results and Discussion

3.1. Biochar and Soil/BC Mixture Characteristics

The BC specific surface area (reactive surface area per unit weight of soil) was 9 m^2 g^{-1}. The BC morphology was diverse due to it being a mixture of three different biochars—sawdust of mixed woods, elephant grass, and sugar cane leaves (Figure 1). Total porosity was 0.0112 cm^{-3} g^{-1} with an average pore size of approximately 200 µm. The particle surface texture was irregular, with micropores (<20 A) accounting for 87% of the total porosity, while mesopores (between 20 to 500 Å) were 13%. Macropores were lacking.
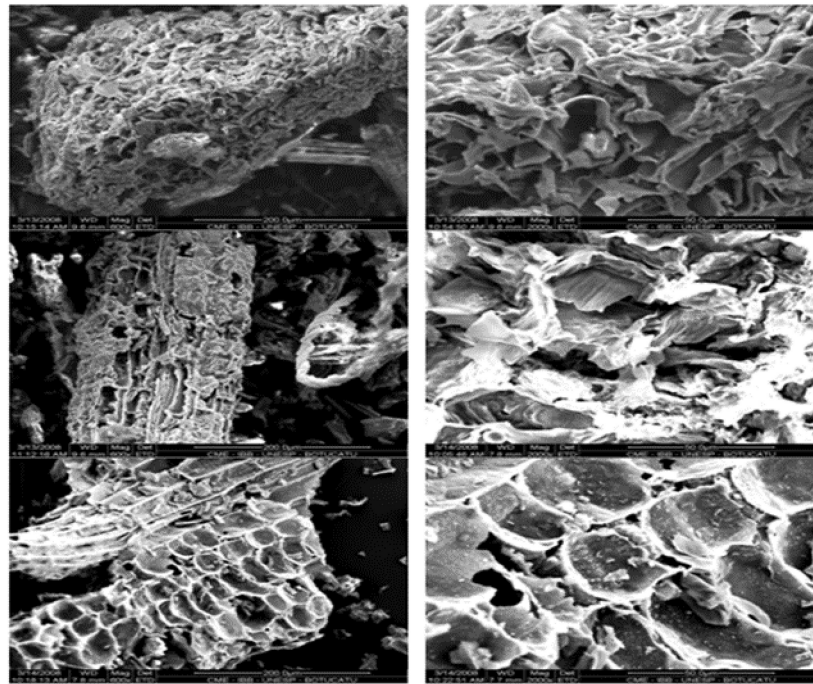
Figure 1. Scanning electron micrograph images for the three different types of particles that composed the fast pyrolysis biochar, expanded 600 times (**left**) and 2000 times (**right**).

These properties are related to the BC's capacity to sorb nutrients and to serve as microsites for soil microorganisms [30]. In addition, slow P adsorption increased with specific surface area, micro and meso-porosity, and ferrihydrite impurities [31]. BC functional surface groups with the potential to influence sorption reactions were composed of phenolics (80%), carboxylics (17%), and lactones (3%). Cumulative water extractable Ca, Mg, K, and Na totaled 5835, 1014, 19,713, and 5.835 mg kg^{-1} (Figure 2a), and dissolved organic Carbon (DOC) equaled 23.9 g kg^{-1}. BC was 62% ash with a pH of 9.8. The initial high electrical conductivity of the BC rapidly decreased as it was sequentially leached with water, while the BC pH remained relatively high after an initial decrease (Figure 2b).

Caution should be taken when applying high rates of BC because of its liming effect, as based on our observation that when BC is added to mineral soil, the pH increased from 4.1 to 8.1. The soil pH affects mechanisms of P fixation. For instance, pH at 4.1 chemical fixation occurs by soluble Fe and Al, when the dominate form of phosphate is $H_2PO_4^-$, and for 8.1 the fixation is mostly as calcium-phosphate when it is HPO_4^{-2} [32].

This BC P fertilizer potential is based on it having a total P value equal to 1484 mg kg^{-1} (0.148% P) which would require over 20 metric t ha^{-1} to provide 30 kg total P ha^{-1}. With inorganic P (Pi) being 61% of total P (909 mg kg^{-1}) that amount increases to 33 metric t ha^{-1} (Figure 3).

The Pi content was mainly due to high P concentration of the BC ash [13], and it can be desorbed from biochar fast and continue slowly (Figure 4). In contrast, [33], working with BC made from herbaceous species over a pyrolysis temperature range of 220 to 550 °C found water-soluble P to be from 20% to 80% of total P depending on whether the plants were grown in soil in P-limited versus high legacy P soils, respectively.
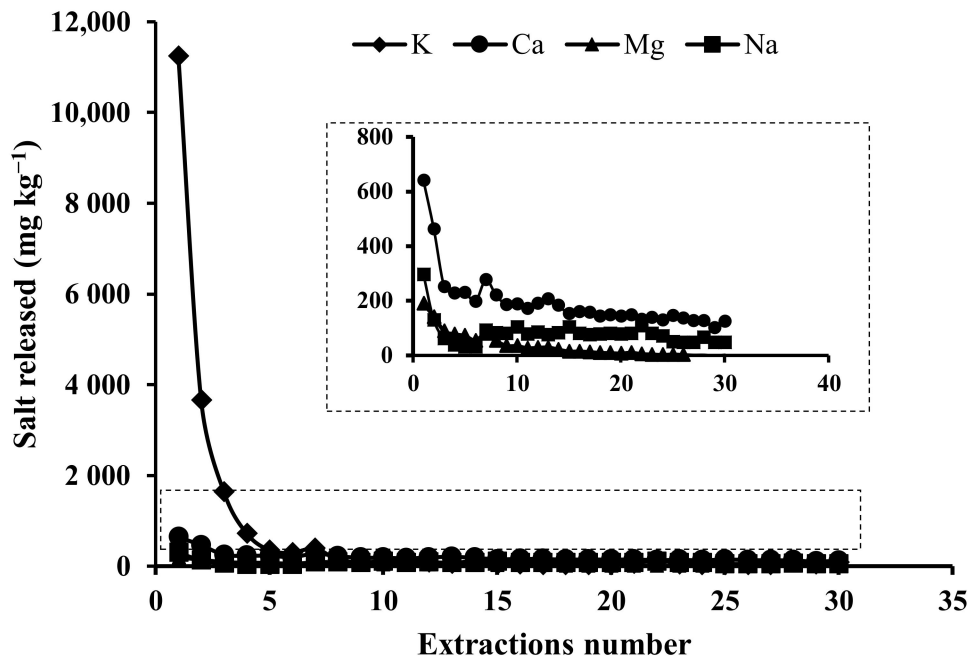
(**a**)
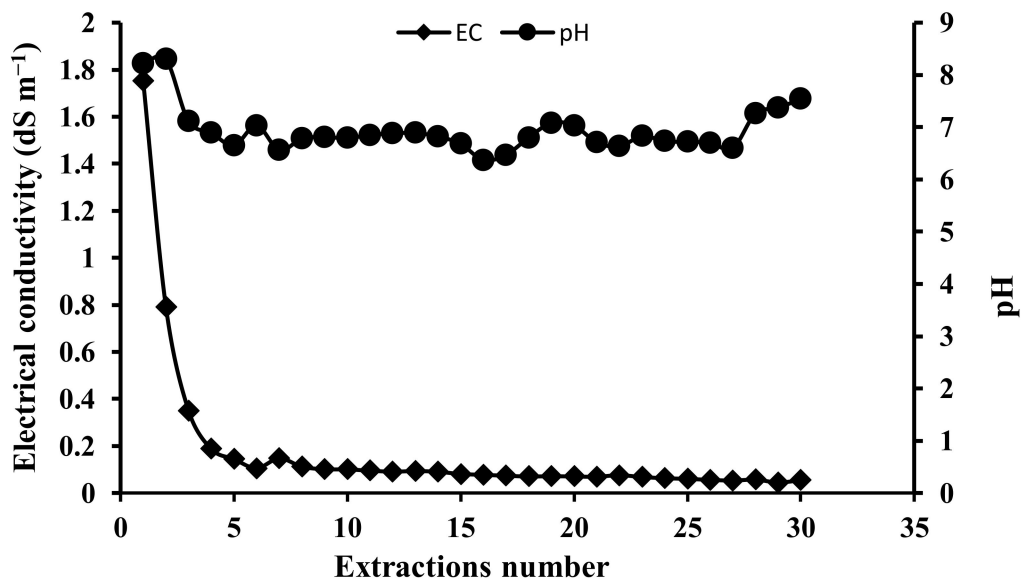
(**b**)

Figure 2. (**a**) Electrical conductivity and pH water extractable (**b**) salts released (Ca, Mg, K, and Na) from fast pyrolysis biochar.
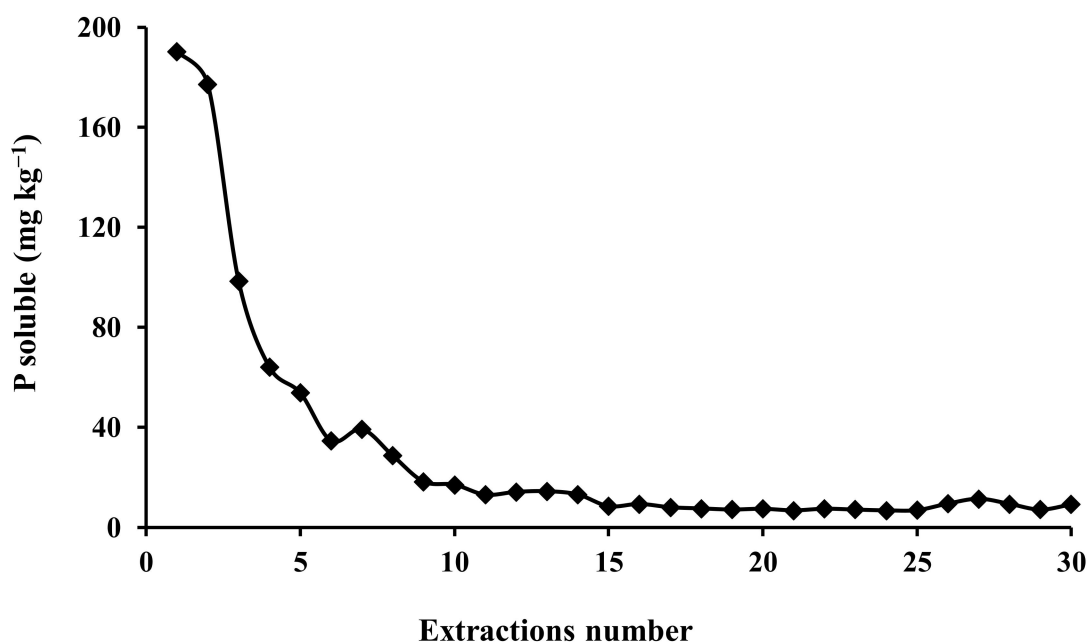
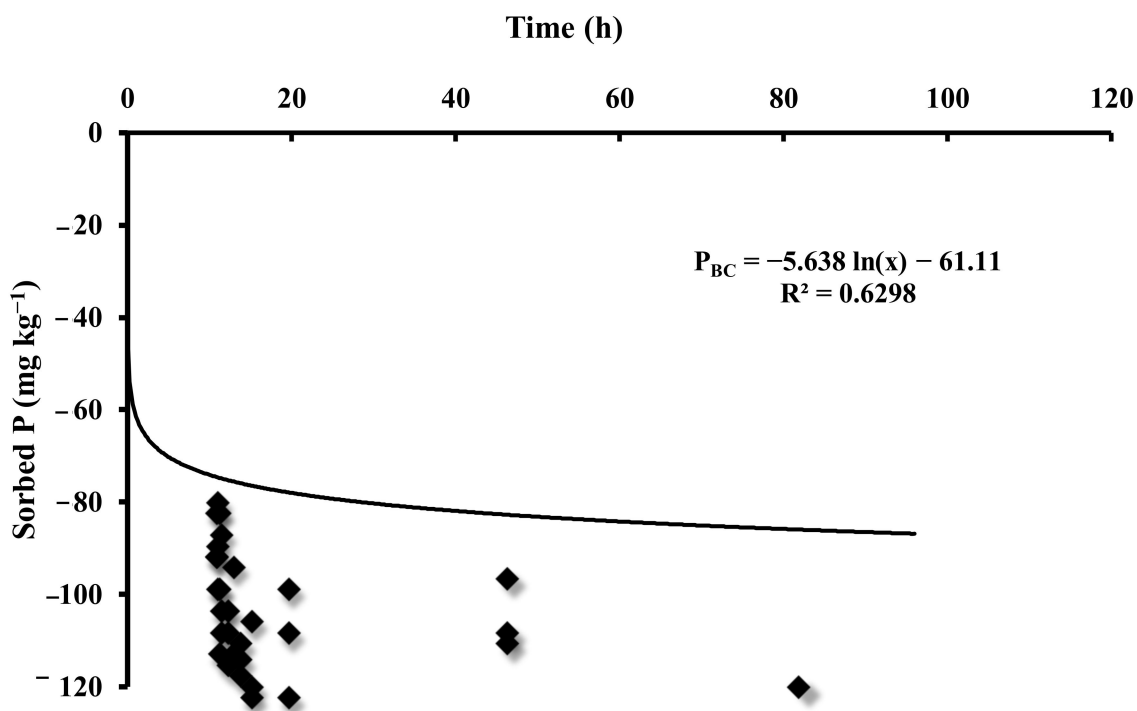**Figure 3.** Water extractable P from fast pyrolysis biochar.

Figure 4. Kinetics of P sorption behavior in fast pyrolysis biochar (BC).

Our data fall within the range described. When plant tissue was warmed, organic C volatilized at around 100 °C. Phosphorus did not volatilize up to 700 °C [34,35]. Thus, all of the P remained in the solid phase and much was converted to inorganic which became water soluble.

In treatment of soil by itself, the P content was 6.0 mg kg^{-1} (Table 1). Low P content was expected in these weathered, acid soils where most P is strongly bounded to hydroxides and oxides of Fe, Al, and Mn [36]. When BC was added to soil, its content rose to 60 mg kg^{-1}

(Table 1) or approximately equivalent to 123 kg P ha^{-1}. Other studies also suggested enhanced P availability in a BC amended soil, which could result in crop production [37].

Incorporation of organic materials into soils effect soil P sorption. In most cases, these effects are attributed to the introduction of DOC [38]. The DOC attributed to the addition of BC was 23.9 g kg^{-1}, giving this material in this soil the distinct potential to decrease P sorption as DOC competes for sorption sites, making P bioavailable.

3.2. Sorption Kinetics

Chemical reactions naturally tend towards equilibrium; the same is true for the P in soil and P in SBC system. This happens when the reaction rate between Pi and soil exceeds the reaction rate between soil and Pi, becoming equal, reaching the equilibrium condition [39]. For the P in soil, the equilibrium condition was reached at 12 h and for the P in the SBC system at 48 h (Figure 5a).

Phosphorus sorption in both cases, S and SBC, had a relatively fast initial reaction that took place between the initial 0 to 30 min for SBC, 0 to 1 h to SBC minus BC (SBC−BC), and 0 to 1.5 h to S. This was followed by a slower sorption reaction (Figure 5b). Probably because P is initially sorbed onto charged external surfaces of soil system during the period of fast P sorption and then diffuses into the BC particles, where slow and constant sorption takes place.

Brazilian tropical Latosol soils are characterized by a high-level P-fixing capacity that is relative to their clay content [40].

P sorption between S, SBC, and SBC−BC was different under the P sorption (*p* = 0.00) and times (*p* = 0.0082) until 12 h. In addition, the P sorption soil and BC effect on SBC was differentiated, under the times up to 12 h, but soil sorption and SBC−BC had the same behavior (Figure 5b).

Sorption has been described as a two-step mechanism: (i) Moieties in an SBC system sorb to external surface sites and rapidly balance with the surrounding solution [41,42]; (ii) then these moieties slowly diffuse to interior sites [43]. In other words, the effect of adding BC to soil should be to decrease the affinity of P to the soil's Fe-oxides and increase soil solution concentrations, thus enhancing P bioavailability [18].

The Le Chatelier's principle corroborates with this statement, if a system in equilibrium (S) is subjected to a "perturbation" (SBC), in this case addition of Pi and OM by BC, which changes any factor (bioavailability of Pi, sorption sites, and pH) that determines the steady state, the system will react by minimizing the disturbance effect (SBC−BC) (Figure 5b) after 12 h of S and SBC−BC presenting the same behavior.
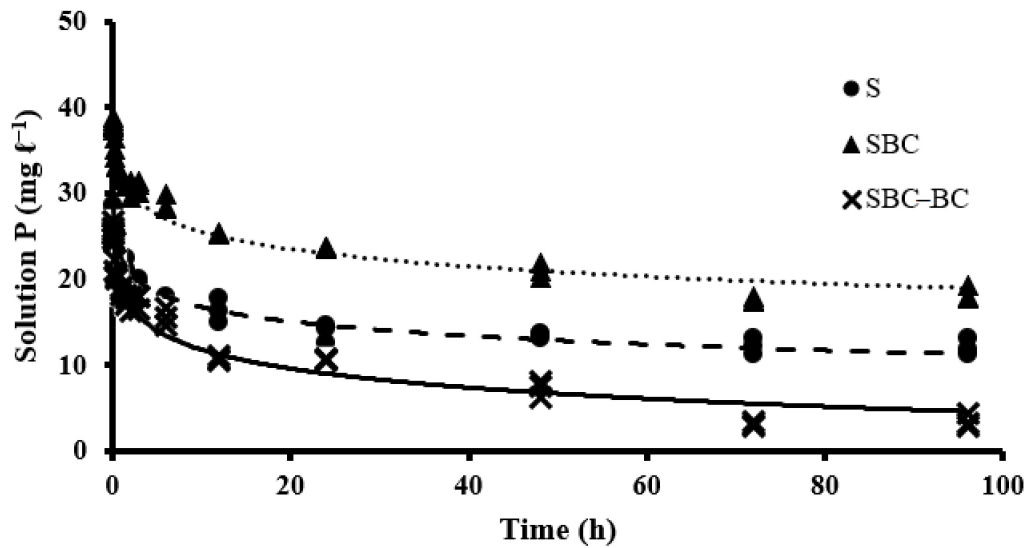
The P sorption rate was equal for the SBC complex and S by itself: Both depended on the amount of soil surface, and the reaction between soil and phosphate involved more than one step, ultimately being controlled by the slower reaction (Figure 6). When comparing S and SBC, the sorption-limiting step appeared to occur after the "initial sorption" step. The reactions in both cases were fast at the first and then became slower and tended to continue; only the sorption capacity was different. This suggested that SBC mixture did indeed differ in the kind of adsorbing surface present (Figure 1) and not only on the amount of site surface (Barrow, 1983) or the amount of P in the BC.

The Boehm titration results corroborated with this statement, showing an increase of 63%, 14%, and 43% in carboxyl, lactone, and phenol functional groups with biochar addition. In addition, these results were consistent with those of [13,44], who found that incorporating biochar with an acid soil increased the equilibrium solution P concentration.
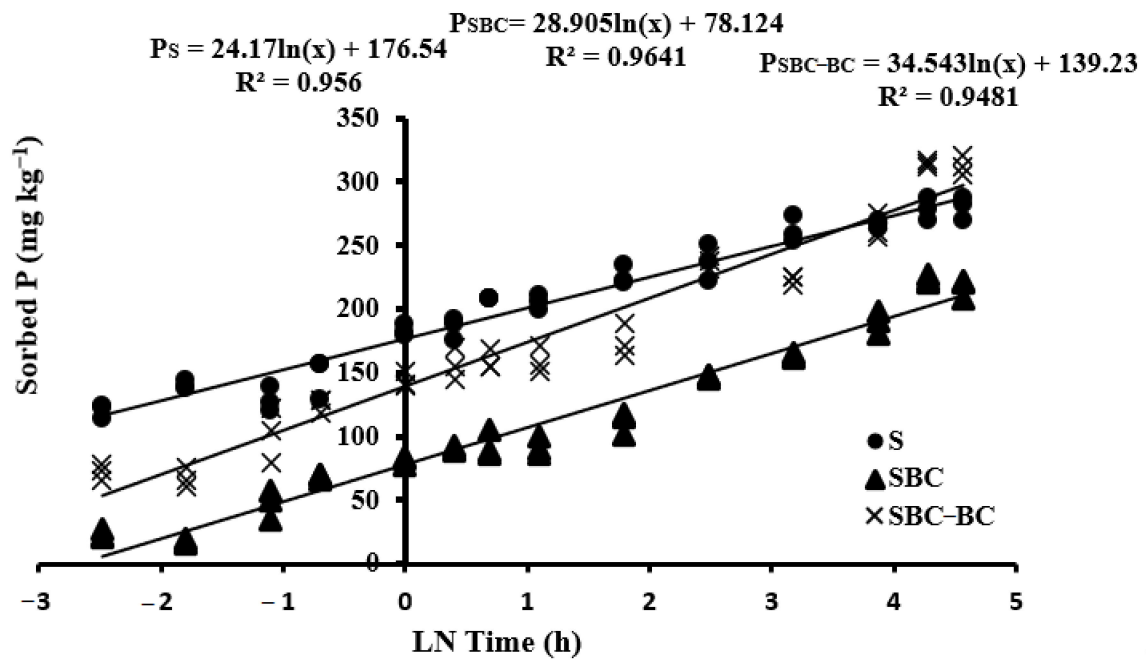
In other words, adding biochar to soil decreased soil P sorption compared to the mineral soil alone. Three separate hypotheses have been used to explain similar results: (i) Inorganic phosphorus desorbed from biochar (Figure 4) was resorbed onto the mineral soil; (ii) charcoal particles physically covered P sorption locations on the soil (Figure 1); (iii) the pH increased when BC was added SBC and the soil surface became more negatively charged, thus increasing anion repulsion and decreasing P sorption [11,13,32,45,46]

$$P_S = -2.417\ln(x) + 22.346 \quad P_{SBC} = -3.182\ln(x) + 19.158 \quad P_{SBC-BC} = -2.9\ln(x) + 32.213$$
$$R^2 = 0.956 \qquad\qquad R^2 = 0.9578 \qquad\qquad R^2 = 0.9635$$

(a)

$$P_{SBC} = 28.905\ln(x) + 78.124$$
$$P_S = 24.17\ln(x) + 176.54 \qquad R^2 = 0.9641 \qquad P_{SBC-BC} = 34.543\ln(x) + 139.23$$
$$R^2 = 0.956 \qquad\qquad\qquad R^2 = 0.9481$$

(b)

Figure 5. (**a**) Soil solution concentration in a Latossolo Vermelho distrofico (Brazilian Soil Taxonomic System; or a Typic Kandiudult in the U.S. System); (**b**) sorption kinetics in a Latossolo Vermelho distrofico (Brazilian Soil Taxonomic System; or a Typic Kandiudult in the U.S. System). Soil = S, soil/BC mixture = SBC, and SBC minus BC = SBC−BC. The area outlined by a dotted rectangle indicates the zone where the reaction appears to become linear.
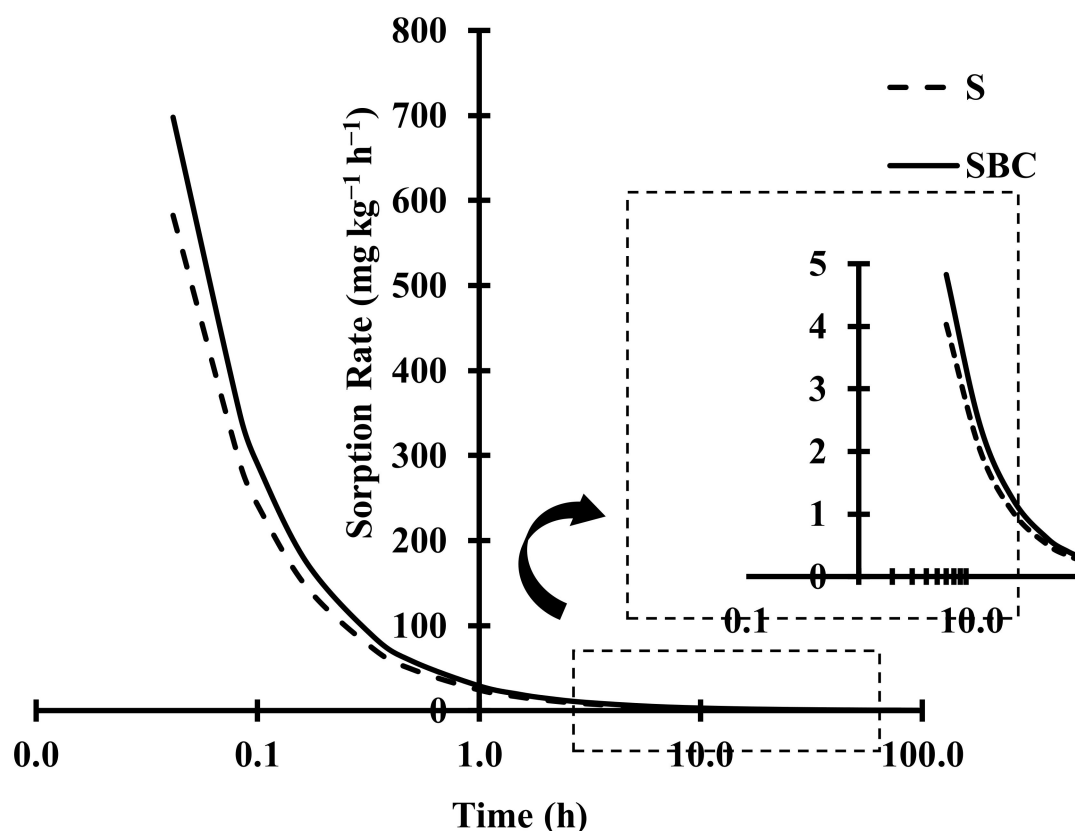
Figure 6. Phosphorus sorption ratio of soil and soil/BC mixture.

4. Conclusions

The kinetics of sorption in the presence of BC showed that the soil solution P concentrations remained higher, which made P more bioavailable for a longer period of time. The BC reduced P sorption onto soil due to: (i) BC covering the potential P sorption sites, (ii) BC desorbing inorganic phosphorus that was resorbed onto the mineral soil, and (iii) BC increasing soil pH and the soil surface becoming more negatively charged. Biochar can be an alternative for P management in tropical soils.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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