

PHOSPHORUS AVAILABILITY IN SOIL INCUBATED WITH BIOCHAR: ADSORPTION STUDY¹

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ABSTRACT - Considering the losses of phosphorus (P) in the soil by the adsorption process and that the use of biochar seems promising from the agricultural point of view, the aim of this research was to evaluate P adsorption by the Ultisol incubated with different biochar doses through kinetic and isothermal study. The experiment was carried out with poultry litter biochar pyrolyzed at 350 °C. Ultisol was incubated with increasing biochar doses, from 0.0 to 61.95 t ha⁻¹. After 60 days, the phosphorus adsorption rate, kinetics and adsorption isotherms were evaluated. The results showed that the soil had the highest capacity to adsorb phosphorus (1.105 mg g⁻¹). Biochar was not a good P adsorbent; regardless of the applied doses, it released P to the equilibration solution. Langmuir model was better at describing the adsorption of P. The pseudo-second order model fitted well to the adsorption kinetics of P, showing that the adsorption is chemically controlled. These results suggest that biochar can increase the availability of P, limiting adsorption; therefore, it could be used as a fertilizer and/or soil conditioner.

Keywords: Adsorption isotherms. Poultry litter. Kinetics. Physicochemical properties.

DISPONIBILIDADE DE FÓSFORO NO SOLO INCUBADO COM BIOCÁRVÃO: ESTUDO DE ADSORÇÃO

RESUMO - Considerando as perdas de fósforo (P) no solo pelo processo de adsorção e que o uso do biocárvão parece promissor do ponto de vista agrícola, objetivou-se com este estudo avaliar o processo de adsorção de P pelo solo Argissolo incubado com diferentes doses de biocárvão através de estudo cinético e isotérmico. O experimento foi realizado com biocárvão de cama de aviário pirolisado a 350 °C. O Argissolo foi incubado com doses crescentes de biocárvão, de 0,0 a 61,95 t ha⁻¹. Após 60 dias, foram avaliadas a taxa de adsorção de fósforo, e cinética e isotermas de adsorção. Os resultados mostraram que o solo apresentou a maior capacidade de adsorção de fósforo (1,105 mg g⁻¹). O biocárvão não foi um bom adsorvente de P; independente das doses aplicadas, liberou P para a solução de equilíbrio. O modelo de Langmuir foi o melhor para descrever a adsorção de P. A cinética de adsorção de P se ajustou bem ao modelo de pseudo-segunda ordem, mostrando que a adsorção é controlada quimicamente. Esses resultados sugerem que o biocárvão pode aumentar a disponibilidade de P no solo, limitando a adsorção, portanto, pode ser usado como fertilizante e/ou condicionador de solo.

Palavras-chave: Isotermas de adsorção. Cama de aviário. Cinética. Propriedades físico-químicas.

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INTRODUCTION

Brazil stands out for its poultry production. According to the Brazilian Institute of Geography and Statistics (IBGE), in 2019 the Brazilian production of chicken carcass was 13,576.976 tons, keeping the country in the position of the world's largest exporter and the second largest producer of meat.

After disinfection, the poultry litter (PL) waste generated by the poultry sector can be reused in another poultry flock or can be used in other activities, for example as agricultural fertilizer since the poultry litter contains high levels of organic carbon (OC), nitrogen (N), phosphorus (P), potassium (K), and other plant nutrients (GUO; SHEN; HE, 2012).

However, the soil application of PL can increase the risk of natural water pollution due to the excessive loss of various nutrients in the soluble form of PL, such as P, corroborating Guo, Shen and He (2012). These authors observed that 12–20% of the P in PL was water soluble and was lost in five rainfall events after soil application. To reduce the rate of P losses, it would be interesting to transform PL into a more stable and slow-release nutrient source, for example, biochar through the pyrolysis process, under limited air supply and temperature above 300 °C. (MOHAN et al., 2014).

The conditions under which biochar is produced can influence the availability of phosphorus. According to Lehmann and Joseph (2009), the specific surface increases as a function of the pyrolysis temperature and the functional groups decrease. These changes can influence the adsorption and consequently the availability of phosphorus. There is evidence to indicate that biochar can decrease the adsorption of P in the soil, resulting in greater availability of the added inorganic phosphate (MORALES et al., 2013). In addition to phosphorus, it was found that the application of poultry litter biochar in an Oxisol increased the levels of potassium, calcium, magnesium, sodium and cation exchange capacity, as well as increasing the pH and decreasing the potential acidity of the soil (FERNANDES et al., 2018).

It is known that the adsorption of P in soils is controlled by the presence of iron (Fe) and aluminum (Al) oxides, which occur mainly in highly weathered soils (QAFOKU et al., 2004). One way to minimize this problem is to increase the pH of the soil, because this phenomenon increases the dissociation of hydroxyl (OH) at the ends and surfaces of mineral particles or organic matter, resulting in an increase in their net negative charge and, consequently, reduction in phosphorus adsorption (FERNANDES et al., 2018). Thus, it is believed that, when applied to the soil, biochar acts as a fertilizer and, due to its alkalinity, it can act as a soil conditioner, corroborating Cui et al. (2011) and Zhai et al. (2015).

These authors demonstrated that the application of biochar in the soil increased P availability due to both P direct supply acting as a source of P and the reduction of P adsorption on Fe oxides.

However, little is known about the adsorption and/or availability of P after the application of poultry litter biochar to the soil. Thus, as a hypothesis, it is believed that this biochar, mainly due to the increase in soil pH, reduces P adsorption, increasing the availability of P in the soil. According to Martinez, Espana and Diaz (2017), after eight consecutive desorptions, the *Eucalyptus globulus* biochar increased phosphorus release compared to the natural soil, between 78 and 84%, thus promoting a greater availability of this element over time.

Phosphorus adsorption can be investigated using kinetic studies (pseudo-first and pseudo-second order) and linear and non-linear isotherms (ZHANG et al., 2015). Commonly used Langmuir and Freundlich models are useful in describing adsorption isotherms and provide effective factors in the prediction of nutrient adsorption characteristics. Thus, the aim of this study was to evaluate the process of P adsorption by the Ultisol incubated with different doses of poultry litter biochar through the kinetic and isothermal study.

MATERIAL AND METHODS

Experiment installation and conduction

The experiment was carried out at the Irrigation and Salinity Laboratory (ISL) of the Agricultural Engineering Department, Federal University of Campina Grande, Paraíba State (PB), Brazil, using an Ultisol collected in the Paraíba State, Brazil (07° 09 '22.42' S; 35° 52' 09.64" W) in the 0-20 cm depth layer. Soil samples were chemically characterized according to Teixeira et al. (2017) and showed the results: pH (H₂O) = 5.35; Ca = 2.78 cmol_c kg⁻¹; Mg = 1.26 cmol_c kg⁻¹; Na = 0.11 cmol_c kg⁻¹; K = 0.17 cmol_c kg⁻¹; H+ Al = 3.27 cmol_c kg⁻¹; organic carbon = 18.8 g kg⁻¹; P = 1.27 mg kg⁻¹ and CEC = 7.59 cmol_c kg⁻¹.

The biochar used in this study was produced in ISL under slow pyrolysis at 350 °C from poultry litter, resulting from the rearing of broilers, with the following chemical attributes: pH = 9.44; EC = 7.33 dS m⁻¹; P₂O₅ = 4.08%; K₂O = 4.35%; Ca = 5.04%; Mg = 1.28%; S = 0.41%; Fe = 0.72%; Mn = 0.05%; Cu = 0.01%; Zn = 0.05%; B = 0.01%; organic carbon = 42.22%; C / N = 18.76 and Zero Charge Point (ZCP) = 8.43. It is an amorphous, porous material, with a predominance of medium-sized pores, approximately 14.8 nm, with a surface area of 3.37 m² g⁻¹. According to X-ray diffraction analyses, feldspar compounds [Orthoclase (KAlSi₃O₈)] and potassium phosphate (K₂(HPO₄)) were identified, confirming the result of the chemical

analysis of the biochar, which had considerable contents of P, K, Ca and Mg. To evaluate the effect of biochar on phosphorus adsorption, the incubation method was used, placing soil samples (0.3 kg) in plastic bags mixed with biochar at the following doses: 0.0, 12.39, 24.78, 37.17, 49.56 and 61.95 t ha⁻¹. The calculation to determine the doses was carried out in order to raise the soil organic matter content in the arable layer (first 20 cm deep) from 18.8 g kg⁻¹ (control treatment) to 25.0, 31.2, 37.4, 43.6 and 49.8 g kg⁻¹. The incubation test was performed with four replications.

In order to promote the release of phosphorus by biochar and the neutralization of soil acidity, increasing doses of biochar were incorporated into the soil samples and incubated for a period of 60 days, keeping their moisture at around 70% with the addition of deionized water. After this period, these samples were used in the kinetic and phosphorus adsorption study.

Phosphorus adsorption kinetics

To evaluate the adsorption kinetics of P, 400 ml of 52.5 mg L⁻¹ solution of P in were added Erlenmeyer flask containing 5 g of soil incubated with different doses of biochar. The samples were left on a horizontal shaker at 120 rpm, at 25 ± 2 °C for 48 hours. During this period, 20-ml aliquots of the samples were taken at the intervals 0.1, 0.2, 0.3, 0.5, 1.1, 1.5, 2.0, 3.0, 6.0, 12.0, 24.0 and 48.0 h, filtered and, by colorimetry, P was measured according to Braga and Defelipo (1972). The experiment was carried out in duplicate.

The efficiency of the process was determined according to Equation 1 and the amount of adsorbed metal was calculated according to Equation 2.

$$T = \frac{(C_0 - C_t)100}{C_0} \quad (1)$$

$$q_e = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where: T is the phosphate ion removal rate (%); C₀ is the initial concentration of the phosphate ion in the solution (mg L⁻¹); C_t is the equilibrium concentration of phosphate ions after adsorption (mg L⁻¹); q_e is the amount adsorbed by mass of adsorbent (mg g⁻¹); V is the volume of effluent (L); m is the mass of the adsorbent (g).

To represent the experimental kinetic data of phosphorus adsorption by the incubated soil, the kinetic models of pseudo-first (LAGERGREN, 1898) and pseudo-second order (HO; WASE; FORSTER, 1996) were used, according to Equations 3 and 4, respectively.

$$q_t = q_e(1 - e)^{-K_1 t} \quad (3)$$

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \quad (4)$$

where: K₁ and K₂ are the adsorption rate constants of pseudo-first (h⁻¹) and pseudo-second order (g mg⁻¹ h⁻¹), respectively; q_t is the amount adsorbed per gram of adsorbent at any time t (h) (mg g⁻¹), q_e is the amount adsorbed per gram of adsorbent at equilibrium (mg g⁻¹) and t represents time (h). The values of q_e, K₁ and K₂ were estimated using the non-linear regression method, using a SOLVER tool, following the sum of squared errors methodology (FOO; HAMEED, 2010).

Adsorption isotherm

The remaining phosphorus (Prem) was determined by stirring a solution of 60 mg L⁻¹ of P in 0.01 mol L⁻¹ CaCl₂ at 120 rpm, for one hour, in a 1:10 ratio of soil:solution (ALVAREZ; FONSECA, 1990). After stirring, the solid and liquid phases were separated, and the concentration of P was determined in the equilibration solution, using the ascorbic acid method, modified by Braga and Defelipo (1972). The doses for determining the Maximum Phosphorus Adsorption Capacity (MPAC) were calculated based on the Prem content and ranged from 0 to 150 mg L⁻¹ (ALVAREZ; FONSECA, 1990). After 24 hours of stirring, the samples were filtered and the phosphorus in the equilibration solution was quantified by colorimetry (BRAGA; DEFELIPO, 1972).

To describe the P adsorption phenomenon, the Langmuir (Equation 5) and Freundlich (Equation 6) equations were used.

$$q_e = \frac{q_m C K_L}{1 + K_L C} \quad (5)$$

$$q_e = K_f C^{1/n} \quad (6)$$

where: q_e is the amount adsorbed at equilibrium (mg g⁻¹), C is the concentration of adsorbate at equilibrium (mg L⁻¹), q_m corresponds to the maximum adsorption capacity (mg g⁻¹), 1/n is the constant related to the surface heterogeneity, and K_L and K_f are the Langmuir adsorption energy constants (L mg⁻¹) and the Freundlich adsorption capacity constant (L mg⁻¹), respectively.

Statistical analysis

For the phosphorus removal rate, the splitting of biochar doses within each level of phosphorus

added was analyzed by the Scott-Knott test using the SISVAR 5.7 statistical software. The fit of equations 1 and 2 to the experimental data was performed by non-linear regression using the Microsoft Office Excel SOLVER tool, following the sum of squared errors methodology, which represents the sum of the squared differences between the experimental and calculated values (FOO; HAMEED, 2010).

The quality of the fits of the adsorption and kinetic models was determined by comparing the values of the determination coefficients (R^2) and sum of squared errors (SSE). The models with the highest R^2 and the lowest SSE were considered the most

suitable to describe the adsorption and kinetic processes.

RESULTS AND DISCUSSION

Phosphorus sorption

The highest rates of P removal, after 24 hours, regardless of the concentration of P applied, were obtained using the soil in the absence of biochar, whose removals were greater than 60% up to the addition of 52.5 mg L⁻¹ of P (Figure 1).

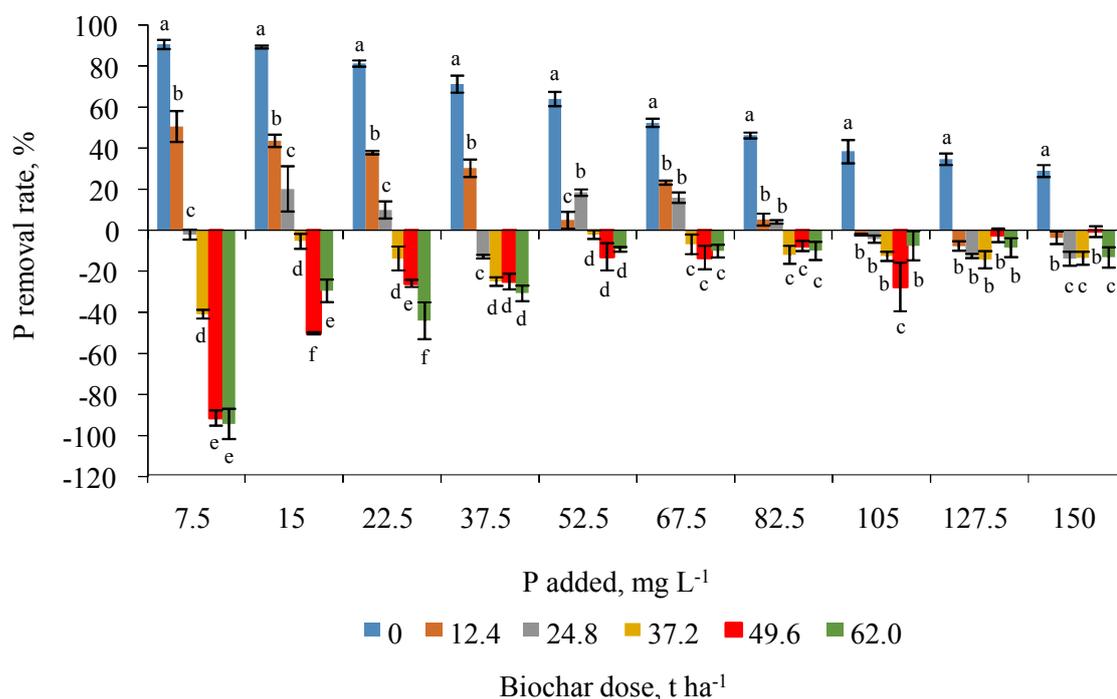


Figure 1. Rates of P removal at different concentrations used in the study of adsorption by soil incubated with biochar doses, after 24 hours of stirring. Means followed by the same lowercase letter indicate that the doses of biochar do not differ from each other within the same concentration of P. Vertical bars represent the standard errors for means of each treatment (n=4).

The capacity of the soil to remove P varied with the doses of biochar and its concentrations in the treatment solutions. In general, the rate of P removal decreased from the moment the soil was incubated with biochar, assuming negative values, regardless of the concentration of P added, with the use of biochar doses greater than 24.8 t ha⁻¹. This behavior indicates that the soil with these doses was not able to remove P because, above these doses, the concentration of P in the equilibrium solution exceeded the capacity of the soil to remove P, so it remained in the solution.

With the increase in the concentration of P in solution, there was a decrease in the removal of P with the use of the highest doses of biochar (Figure 1). This occurred probably for the same reason as before, that is, the soil removal capacity also

decreased with the increase of the concentration of P in the soil solution (P added by the treatment solution + P released by the biochar), increasing the P in equilibrium. Taking as an example the application of 150 mg L⁻¹ of P, the remaining P concentration corresponded to 106.64, 155.50, 173.33, 170.36, 150.96 and 169.89 mg L⁻¹ of P with the application of 0, 12.4, 24.8, 37.2, 49.6 and 62.0 t ha⁻¹ of biochar, respectively. In this case, only in the control treatment (absence of biochar) was P removed, thus characterizing the adsorption of this element by the adsorbent (soil). These results corroborate Yao et al. (2011), who demonstrated that biochar without pre-treatment (without chemical modifications) has a very high negative zeta potential, so anions from P, such as phosphate, are not adsorbed.

Increase in the availability of P, after the application of biochar, was also reported by Bai et al. (2015), who found a significant increase in the release of P to the soil, approximately 1000 times, with the application rate of 10 t ha⁻¹ of poultry litter biochar.

Although most studies have shown that biochar can increase the P content in the soil due to the direct supply of P acting as a source of P and/or the reduction of P adsorption on Fe oxides (CUI et al., 2011; ZHAI et al., 2015), some studies have shown that there is no significant effect and others have shown that biochar can even reduce the available P in the soil, probably due to the characteristics of the raw material used in its production.

So far, variations in the availability of P in soils altered by biochar are not clearly understood. However, it is reasonable to state that the impact of biochar on the availability of P in soils is affected by the characteristics inherent to the biochar (for example, pyrolysis temperature, presence of functional groups, total P content, pH, among others) and the characteristics of the soil, such as soil pH, inorganic and organic soil P, clay minerals, ionic strength and native microbial diversity.

In this work, the pyrolysis temperature used, 350 °C, for the production of poultry litter biochar may have influenced the availability of phosphorus. Zhang et al. (2016) evaluated the influence of nine biochars and different pyrolysis temperatures and found that the biochar of blady grass (*Imperata*

cylindrica) at 450 °C was the one that promoted the highest amount of P available in the soil and only the biochar derived from Mallee (*Eucalyptus polybractea*) at 720 °C showed an extraordinary P adsorption capacity. Glaser and Lehr (2019) reported that biochar produced at temperatures above 600 °C did not promote a significant effect on the availability of P; however, the same behavior was not observed when pyrolysis was performed between 450 and 600 °C, where the availability of P increased significantly in soils incubated with biochar.

The rate of phosphate removal by the soil incubated with different doses of biochar for 48 h is shown in Figure 2. In this study, the concentration of P used was 52.5 mg L⁻¹. It can be seen that, among the various treatments, only the soil samples incubated with the first three doses of biochar showed a positive phosphate removal capacity. However, as seen in the sorption study, there was a decrease in phosphate retention due to the application of biochar; in decreasing order the highest rates were 30.62, 14.08 and 14.08% for treatments 0, 12.4 and 24.8 t ha⁻¹, respectively. At other doses of biochar, that is, 37.2, 49.6 and 62.0 t ha⁻¹, the phosphate retention was negative since the concentration of this anion increased compared to the initial concentration after the end of the reaction (48 h), whose means were 55.43, 53.08 and 60.13 mg L⁻¹, respectively. This increase was probably due to the blocking of soil adsorption sites and the release of P promoted by biochar.

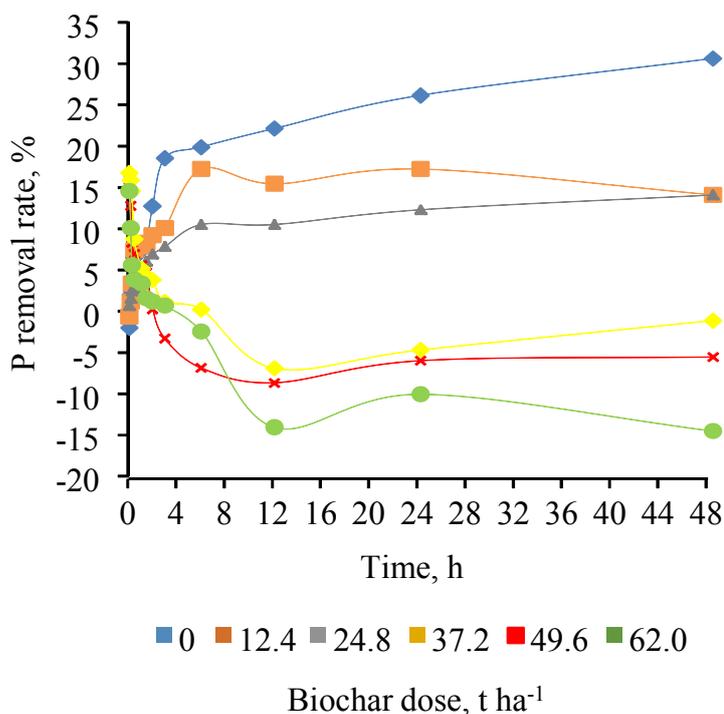


Figure 2. Phosphorus removal rate over time as a function of the application of different biochar doses

Phosphorus adsorption kinetics

The adsorption behavior of P as a function of contact time in treatments 0, 12.4 and 24.8 t ha⁻¹ of biochar was investigated through kinetic studies (Figure 3). Regardless of the treatment, the P adsorption process was fast in the initial stage of the reaction due to a high number of binding sites available for adsorption (GHAEDI; HASSANZADEH; KOKHDAN, 2011), then the rate gradually decreased with the contact time until reaching equilibrium, which occurred within 6 h. This time was similar to that observed by Qian et al. (2013), who reported that approximately half of the

P is released as orthophosphate and pyrophosphate at a pH of 9 in the first 8 hours.

Also according to Figure 3, the phosphorus adsorption kinetics (qt) decreased as a function of increasing doses of biochar (0, 12.4 and 24.8 t ha⁻¹), as can be seen, respectively, in the sequence of this figure, A, B and C. This is because, once applied to the soil, biochar releases phosphorus instantly and slowly in the long term, corroborating Li et al. (2019). The order of the amount of adsorption in equilibrium, observed in this study, was consistent with the results of the sorption experiments, corroborating that the soil in the absence of biochar has the highest P adsorption capacity.

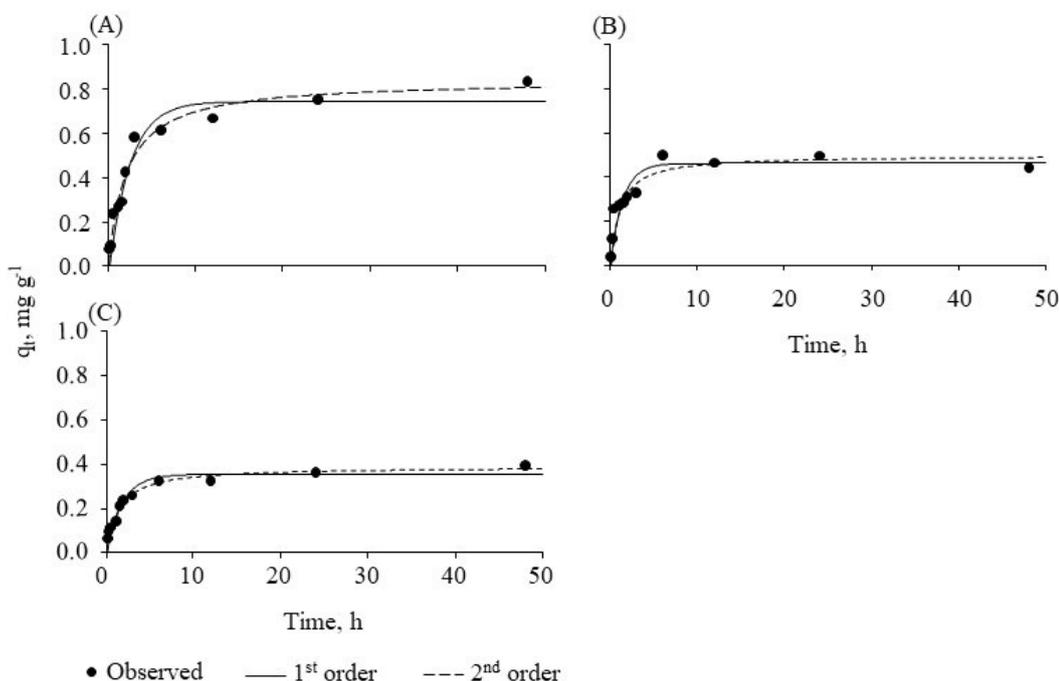


Figure 3. P adsorption kinetics in soil incubated with 0 t ha⁻¹ (A), 12.4 t ha⁻¹ (B) and 24.8 t ha⁻¹ (C) of biochar.

From the curves obtained for the first- and second-order kinetic models, the relevant calculations were performed to obtain the parameters related to the biochar's adsorption kinetics in relation to the studied ion, that is, the values of the velocity

constants, adsorption (k), concentration of metal adsorbed in equilibrium (qe), the coefficient of determination (R²) and the sum of the squared errors (SSE), calculated from the graphs generated for both kinetic models (Table 1), were obtained.

Table 1. Parameters of P adsorption kinetics as a function of biochar doses

Biochar application t ha ⁻¹	Pseudo-first order				Pseudo-second order			
	q _e	K ₁	R ²	SSE	q _e	K ₂	R ²	SSE
	mg g ⁻¹	h ⁻¹			mg g ⁻¹	g mg ⁻¹ h ⁻¹		
0	0.747	0.414	0.958	0.046	0.839	0.583	0.969	0.036
12.4	0.463	0.701	0.926	0.031	0.497	2.075	0.940	0.026
24.8	0.355	0.556	0.972	0.007	0.388	1.900	0.986	0.003
37.2	-	-	-	-	-	-	-	-
49.6	-	-	-	-	-	-	-	-
62.0	-	-	-	-	-	-	-	-

As shown in Table 1, both kinetic models fitted to the experimental data; however, considering the values of the determination coefficient (R^2) and the sum of squared errors (SSE), the experimental results of kinetic adsorption, regardless of the dose of biochar, are better explained in terms of the pseudo-second order model, corroborating Wang et al. (2018) and Jung et al. (2015). Based on this model, the calculated values of q_e were close to the experimental values (0.839, 0.443 and 0.397 for doses of 0, 12.4 and 24.8 t ha⁻¹, respectively, after 48h) and also the values of R^2 were close to 1.0.

The pseudo-second order model assumes chemisorption as the predominant stage of the kinetic mechanism of adsorption, involving chemical interactions that lead to the formation of chemical compounds or adsorption complex on the surface of the adsorbent material (OFOMAJA; NAIDOO; MODISE, 2010). In this case, adsorption is related to the concentration of the adsorbent in solution and to the adsorbent adsorption sites, suggesting that the adsorption speed is dependent on the adsorption capacity in equilibrium and not only on the adsorbate concentration.

Regarding the concentration of P adsorbed in equilibrium (q_e), there was a decrease in its values with the increase in the applied dose of biochar; such result indicates that the biochar reduces the P adsorption capacity of the soil. However, this information can only be confirmed by the results obtained from the equilibrium studies, presented later.

Still in relation to Table 1, it appears that the biochar promoted an increase in the adsorption speed (k). This behavior is due to the concentration of P present in the biochar, equal to 40.8 g kg⁻¹ of total P. The adsorption rate increased with the use of biochar due to the release of P in the equilibrium solution; however, despite the higher values of (k), adsorption sites were blocked by the biochar, decreasing the adsorbed concentration.

Adsorption isotherm

Isotherms are mathematical models that describe an adsorption system. Through these models it is possible to evaluate interactions between the material that adsorbs (adsorbent) and the ion that is adsorbed (adsorbate), the ion being retained on the solid interface. In this study, the adsorbent was the soil in the absence of biochar and the one incubated with 12.4 t ha⁻¹ because, as verified in the previous topic on sorption, the release exceeded the adsorption in the treatment of soil + 24.8 t ha⁻¹ of biochar with the addition of the following concentrations: 7.5, 37.5, 105.0, 127.5 and 150.0 mg L⁻¹ of P. At the other doses, sorption was not observed regardless of the added concentration.

The P adsorption isotherms were obtained by the relationship between the amount of P adsorbed (q_e , mg g⁻¹) and the equilibrium concentration (C_e , mg L⁻¹). These isotherms for treatments 0 and 12.4 t ha⁻¹ of biochar were evaluated by fitting with the Langmuir and Freundlich models (Figures 4A and 4B).

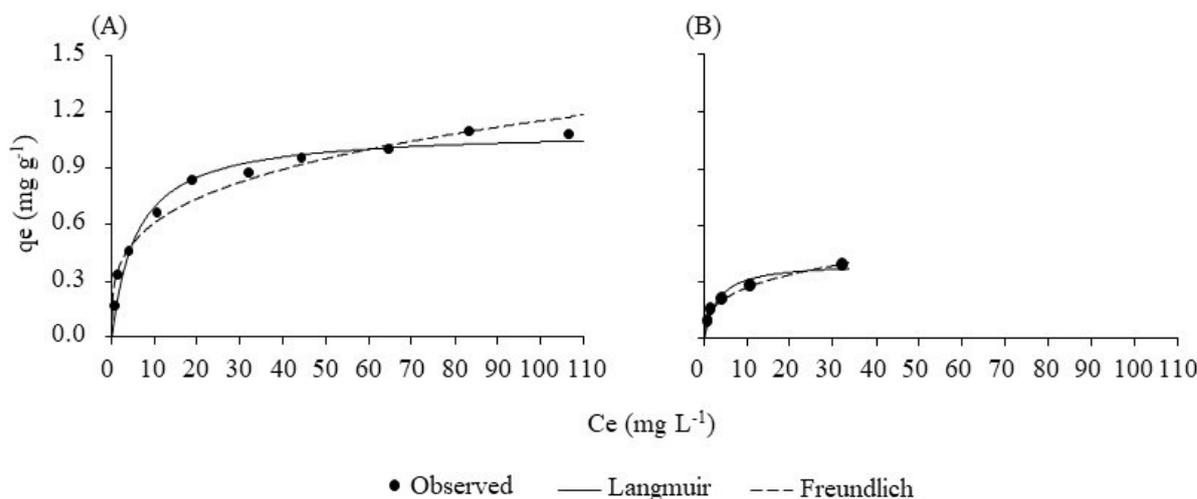


Figure 4. P adsorption isotherms in the soil incubated with 0 t ha⁻¹ (A) and 12.4 t ha⁻¹ (B) of biochar.

Still analyzing Figures 4A and 4B, it was noticed that the adsorption isotherms, regardless of the applied biochar dose, showed a concave curvature in relation to the abscissa, indicating that the adsorption was favorable, with the adsorbent surface having a high affinity for the ion in study,

even under conditions of low concentration in the solution. There was also a decrease in the availability of adsorption sites with the increase in the concentration of the solution.

The values of the maximum phosphorus adsorption capacity (q_{max}) and the adsorption

energy constant (K_L) for the Langmuir isotherm, the adsorption capacity constant (K_f) and the constant (n) for the Freundlich isotherm, the coefficients for determining the equations and the sum of the squared errors (SSE) of the models are shown in Table 2.

The Langmuir and Freundlich isothermal models were fitted to the P adsorption data. Regardless of the applied dose, both models described the P adsorption patterns well, evidenced by the high values of determination coefficient (R^2) and low values of sum of squared errors (SSE). However, in the absence of biochar treatment, the Langmuir model showed the highest coefficient of determination (0.986) and the lowest sum of squared errors (0.022), showing that P adsorption was better described by this model, assuming that sorption was uniform on all the binding sites. With the application of 12.4 t ha⁻¹ of biochar, the Freundlich model showed an R^2 equal to 0.993 and an SSE of 0.0007, indicating that the adsorption occurred with the formation of multilayers, instead of just one monolayer, and that affinity for adsorption sites decreased exponentially with increased saturation

(PAUL, 2013).

The maximum phosphorus adsorption capacity (q_{max}) decreased with the use of biochar, from 1.105 mg g⁻¹ (absence of biochar) to 0.402 mg g⁻¹ (soil plus 12.4 t ha⁻¹ of biochar), which represented a 63.62% reduction in the capacity of the soil to adsorb phosphorus (Table 2). Unlike q_{max} , the Langmuir binding energy (K_L) increased as a function of the application of the biochar, from 0.174 to 0.328 L mg⁻¹ with doses 0 and 12.4 t ha⁻¹, respectively, indicating that at the lowest incubation rates the P was adsorbed more strongly by the incubated soil. However, this result is not conclusive, because only at the lowest dose of application of biochar was it possible to determine the isotherms and, even so, adsorption occurred only at 5 of the 10 concentrations added. Novais et al. (2018) also using biochar from poultry litter pyrolyzed at 350 °C, found values of q_{max} higher than that observed in this study, which corresponded to 250 mg g⁻¹, but the authors only verified adsorption by the biochar after doping with MgCl₂.

Table 2. Parameters of the P adsorption isotherm according to the application of biochar for the Langmuir and Freundlich models (SSE = Sum of squared errors).

Biochar application t ha ⁻¹	pH	Parameters estimated by Langmuir equation				Parameters estimated by Freundlich equation			
		q_m mg g ⁻¹	K_L L mg ⁻¹	R^2	SSE	K_f L mg ⁻¹	n	R^2	SSE
0	5.20	1.105	0.174	0.986	0.022	0.017	3.614	0.972	0.042
12.4	5.56	0.402	0.328	0.971	0.003	0.002	3.087	0.993	0.0007
24.8	5.92	-	-	-	-	-	-	-	-
37.2	6.20	-	-	-	-	-	-	-	-
49.6	6.35	-	-	-	-	-	-	-	-
62.0	6.50	-	-	-	-	-	-	-	-

The decrease in P adsorption may be related to the increase in soil pH after the application of biochar, corroborating Cui et al. (2011). In Table 2, it can be seen that in the control treatment the soil pH was 5.20, but its value increased proportionally with the use of biochar, reaching its highest (6.50) with the use of 49.8 g kg⁻¹. The Ultisol used in this study, for being very weathered, has its electrical charges dependent on pH, so the increase of this attribute with the use of biochar increased the content of negative net charge in the soil and consequently decreased the adsorption of phosphorus.

According to Wei et al. (2013), the labile P concentration of the biochar increases proportionally with the acidity of the soil. When the pH of the soil increases in response to the addition of biochar, the increase in the negative charge on the mineral surface of the soil favors the decrease in the adsorption of P (MURPHY; STEVENS, 2010). As a result, there is an increase in the availability of phosphorus in the soil (CUI et al., 2011). This occurs when Ca and Mg activities are low enough to prevent

Ca / Mg-P precipitation (QIAN et al., 2013).

Still in relation to Table 2, it is observed that the adsorption capacity (K_f) and the Freundlich constant (n) were greater in the treatment with absence of biochar, 0.017 and 3.614, respectively. According to Kim et al. (2018), n values between 1 and 10 indicate that the adsorption was effective and, as the K_f value increases, the affinity of the adsorbate for the adsorbent increases. These results demonstrate that the Ultisol used in this study, when incubated, has a smaller sorption site for P. Mahadevan et al. (2018) reported that the n values varied from 0.7 to 2.5 for the removal of P by the bentonite-alum system. According to Novais et al. (2018), the n values ranged from 1 to 3 for adsorption of P in poultry litter biochar and sugarcane bagasse.

Despite the fact that the poultry litter biochar used in this study has characteristics that could promote an adsorption of P such as surface area (3.37 m² g⁻¹) and presence of mesopores, such characteristics did not increase its adsorptive

capacity for the ion phosphate. On the contrary, an increase in P available to the soil was observed as a function of biochar doses, probably due to its alkaline character, increasing the presence of negative charges in the soil, and due to the release of P from its composition to the soil. The isothermal and kinetic results of this study suggest that the application of biochar decreases the phosphorus adsorption capacity of the Ultisol and increases the concentration of remaining P, which is promising from an agronomic point of view as it increases the availability of this nutrient to crops

CONCLUSIONS

The highest phosphorus adsorption capacity in the soil was 1.105 mg g^{-1} , confirming the kinetic study, where there was a decrease in adsorption, proportionally due to the application of biochar, whose released concentration surpassed the adsorbed one, incubating the soil with 37.2, 49.6 and 62.0 t ha^{-1} .

The Langmuir model was better at describing the adsorption of P by the soil in treatments with 0 and 12.4 t ha^{-1} of biochar.

The pseudo-second order model fitted well to the adsorption kinetics of P, showing that the adsorption is controlled chemically.

Considering that, in weathered soils with low P content, poultry litter biochar could be used as fertilizer and as soil conditioner, increasing the availability of P to the soil.

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