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Kinetics and Thermodynamics of Phosphorus Sorption on Goethites: Effects of Biochar Application

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Abbreviations: Al, aluminum; BET (batch equilibration technique); Fe, iron; P, phosphorus.

ABSTRACT

Bioavailability of phosphorus (P) in soils is controlled by, inter alia, the presence of Fe and Al oxides, which readily bind with P. Biochar has been suggested for minimizing P sorption to oxides and, therefore, improving P availability to plants. However, the kinetics and temperature dependence of biochar influence on P sorption are poorly understood. The objective of this study was, therefore, to determine the kinetics and thermodynamics of P sorption by goethite as affected by biochar application at 0 and 40 g kg⁻¹ oxide. Batch equilibration tests were run at 15, 25, and 35°C, and solution P concentrations were measured 0.5, 1, 3, 6, 9, 12, and 24 h after the start of incubation. Sorption of P by the oxides followed pseudo-first-order kinetics. Biochar application enhanced cumulative P sorption by both oxides, and the increase was greater for Al-goethite. Phosphorus sorption increased as temperature increased from 15°C to 25°C but declined at 35°C. Phosphorus sorption on biochar-amended oxides was associated with low activation energy (E_a) values, indicating that the sorbed P in soils containing goethite and Al-goethite could still be plant available. This information will contribute towards a better understanding of processes affecting biochar effects on P fate in soils.

The management of P to maximize crop yields while minimizing environmental contamination is critical (Cordell et al., 2011). It is well-known that the bioavailability of P in soils is controlled by, inter alia, the presence of iron (Fe) and aluminum (Al) oxides, which are found in almost all soils but are dominant in highly-weathered soils (Qafoku et al., 2004). Goethite (α -FeOOH) is the main oxide in these soils, but the Fe in the goethite structure can be substituted by a large number of cations, mostly Al due to its abundance in rocks and soils, and its mobilization with Fe during the weathering process (Cornell and Schwertmann, 2003; Qafoku et al., 2004). Phosphorous sorption onto goethite occurs due to the crystal morphology and high specific surface area of these minerals (Ruan and Gilkes, 1996; Cornell and Schwertmann, 2003; Hua et al., 2012). Factors influencing the rate of P sorption on goethites are pH (Barrow, 1984; Antelo et al., 2005; Persson et al., 2012), solution ion composition (Antelo et al., 2005; Weng et al., 2012), temperature, time of contact (Barrow, 1983), and organic matter content (Sibanda and Young, 1986; Weng et al., 2012; Fu et al., 2013).

Many studies have examined ways of improving soil fertility by minimizing P sorption by oxides in soils, with one of the promising approaches being the use of biochar (Daza-Torres et al., 2008; Duku et al., 2011). Biochar is a carbon-rich material produced from the pyrolysis of organic materials (Schoumans et al., 2015). The practice of adding biochar to soil originated approximately 2500 years ago in Native American settlements of the Amazon region, Brazil (Atkinson et al., 2010; Duku et al., 2011). Amazon Basin soils are highly weathered and consequently have low fertility (Wambeke, 1992). By adding a mixture of charcoal and nutrient-rich materials to infertile Amazonian soils over many years, a dark soil (locally known as Terra Preta de Indio) was formed (Atkinson et al., 2010; Kookana et al., 2011). The fertility, organic matter content, and cation exchange capacity (CEC) of these soils are significantly higher than

those of adjacent soils (Oxisols) (Liang et al., 2006) due to the active, porous surface properties (Yao et al., 2010) and chemical make-up of the surface groups of biochar (Spokas et al., 2012).

Biochar has been shown to increase P availability and plant productivity (Lehmann et al., 2003; Duku et al., 2011). Cui et al. (2011) reported a 30-40% reduction in P sorption by ferrihydrite, hence increased P availability, following the addition of rice straw-derived biochar. Similarly, Jiang et al. (2015) reported a decrease in P sorption in variable-charge soils amended with crop straw-derived biochar. In contrast, Novak et al. (2009) observed a decrease in leachate P concentration when pecan shell biochar was applied to a loamy sand, suggesting greater sorption with the addition of the biochar. Similarly, wheat straw biochar increased P sorption in an acidic inceptisol (Xu et al., 2014). Parvage et al. (2013) reported that wheat residue biochar can act as a P sink when applied at 20 to 40 g kg⁻¹ soil, whereas at biochar rates of ≤ 20 g kg⁻¹, the biochar had no significant effect. However, other studies found that biochar had no significant effect on P sorption (Soinne et al., 2014) or leachability of P (Iqbal et al., 2015) in amended soils.

Temperature can affect the rate of P sorption and the strength of P bonding in the soil. High soil temperatures may favor fast P sorption (Gardener and Johnes 1973; Chien et al., 1982) and strong P bonding via chemisorption, which requires a high activation energy (Spark 1989; Weber et al., 1991), increasing P fixation by oxides in soil and, therefore, making P less available to crops (Barrow, 1979). On the other hand, low soil temperatures may limit the plant availability of P via decreased desorption (Gardener and Johnes 1973). Thus, an understanding of how temperature affects P sorption in the presence of biochar provides crucial information for effective management of P in soil. This is especially true for Canadian soils where temperature

varies greatly during the growing season, with implications on P availability (Manitoba Soil Fertility Guide, 2007).

To our knowledge, the effects of biochar on the kinetics and temperature dependence of P sorption by goethite – an important constituent of soils – have not been investigated. Therefore, the objective of this experiment was to determine the kinetics and thermodynamics of P sorption by goethite as affected by biochar application.

MATERIALS AND METHODS

Preparation of Oxides and Biochar

Goethite (α -FeOOH) was synthesized following the procedure of Schwertmann and Cornell (2003). Briefly, 180 mL of 5 M KOH were rapidly stirred into 100 mL of a 1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution in a 2-L polyethylene flask. After stirring, the suspension was immediately diluted to 2 L with reverse osmosis (RO) water and left in a 70°C oven for 60 h. The resulting suspension was centrifuged, rinsed with RO water, and then dried in an oven at 60°C for 24 h.

Aluminum-substituted goethite was synthesized by mixing 1 M $\text{Fe}(\text{NO}_3)_3$ and 0.5 M AlCl_3 solutions in a polyethylene flask (Schultze and Schwertmann, 1984; Torrent et al., 1992) and then rapidly stirring in 0.3 M KOH. The solutions were subsequently stored in an oven at 70°C for 14 d. The resulting suspension was centrifuged, washed, and dried for 24 h.

Biochar was obtained from Diacarbon Energy, Inc. (Burnaby, BC) and produced from the pyrolysis of wood chips at approximately 500°C. The chemical composition of the biochar used in this experiment was obtained from manufacture and is listed in Table 1.

Experimental Design

The experiment was laid out as a completely randomized design with a $2 \times 2 \times 3$ factorial treatment structure. The factors were an oxide (Goethite and Al-substituted goethite), biochar rate (0 and 40 g kg⁻¹ oxide), and reaction temperature (15, 25, and 35°C). Reaction times were 0.5, 1, 3, 6, 9, 12, and 24 h. All treatments were replicated three times. A separate set of triplicate blanks containing the background solution were included to quantify the release of P from biochar as a quality control measure.

X-Ray Diffraction (XRD) Analysis and Scanning Electron Microscopy with X-ray Microanalysis (SEM-EDS) of Goethite and Al-substituted Goethite

X-ray diffraction patterns of the samples were analyzed with a Siemens D5000 powder diffractometer (Cu-K α radiation, $\lambda = 1.54178\text{\AA}$) equipped with a scintillation detector and a graphite monochromator, and operated at a tube voltage of 40 kV and a tube current of 40 mA. Step scan data were collected from 3–65° 2 θ using a step-width of 0.02° 2 θ and a dwell time of 1 s step⁻¹. Divergence and anti-scatter slits were both set to 1°. The datasets were subsequently processed using the Jade v9.5 software package and the Powder Diffraction File (PDF-4+ 2012) database.

The technique of X-ray microanalysis with energy dispersive spectroscopy (EDS) was used to measure Al substitution in the goethite structure and to detect impurities (Table 2). This technique allows the determination of amounts up to 1 - 2% of the elements present per volume micrometer of the samples (Dedavid et al., 2007). Goethite and Al-substituted goethite samples were placed on aluminum specimen holder stubs with double-sided carbon tape holding the specimens in place. The samples then received a carbon bath. Samples were observed in a

Scanning Electron Microscope (SEM) LEO EVO 40 PVX and analyzed by a microanalysis X-ray system (Bruker, Madison, WI, USA). Several images were generated for each sample at 20 kV and a working distance of 5.5 to 6.5 mm. The X-ray microanalysis used the energy of 10 kV, accelerating potential of 15.0 kV, and a current ranging from 2.48×10^{-9} to 2.54×10^{-9} A.

X-ray diffraction patterns for the synthesized goethite and Al-goethite show that these oxides have low crystallinity (Fig. 1). The XRD for goethite showed peaks at d values of 4.19, 3.37, 2.69, 2.58, 2.45, 2.25, 2.19 Å, indexed, respectively, to the (110), (120), (130), (021), (111), (121), and (140) planes of pure goethite (JCPDS Card No. 17-0536). For Al-goethite, the d values were 4.18, 3.37, 2.68, 2.57, 2.44, 2.24, and 2.18 Å, with typical peaks of (110), (120), (130), (021), (111), (121), and (140), respectively. Overall, the d-values for these characteristic peaks were smaller for Al-goethite as expected since Al^{3+} (0.53 Å) has a slightly smaller radius than Fe^{3+} (0.65 Å) (Schulze, 1984). The substitution of Al for Fe in the goethite structure will, therefore, cause a decrease in the average size of the unit cell, related to the degree of Al substitution and can be indicated by Al-goethite XRD lines shifting towards smaller d spacings. Potassium (from the background KOH solution) and Al were found in the Fe-goethite as impurities. In contrast, only Fe and Al were detected in the Al-substituted goethite. The synthetic Fe-goethite mainly contained Fe (72%). The results of a semi-quantitative analysis indicated goethite contained 0.69% Al while Al-goethite contained 2.96% Al, confirming greater Al substitution in Al-goethite as expected.

Batch Equilibration Study

A batch equilibration technique was used to investigate the kinetics and thermodynamics of P sorption by goethite and Al-substituted goethite in the presence of biochar. The sample

treatments were prepared by adding 0.1 g of each oxide (goethite or Al-substituted goethite) into 125-mL Erlenmeyer flasks containing 7 mg P L^{-1} in a 100 mL solution of KH_2PO_4 in 0.01 M KCl. Biochar was mixed with each oxide (goethite and Al-goethite) at a rate of 40 g kg^{-1} for treatments receiving biochar. Control treatments received either oxide but no biochar. The experiment was conducted at three temperatures (15, 25, and 35°C) and seven incubation times (0.5, 1, 3, 6, 9, 12, and 24 hours). Additionally, a set of blanks consisting of the background solution only were included as a quality control measure to account for the release of P from biochar. All treatments were replicated three times, resulting in 378 experimental units. The pH of the resulting suspension was immediately adjusted to 5.5 ± 0.5 by adding HNO_3 or KOH solutions. The starting time of the sorption reaction was set just after pH adjustment.

All treatments were allowed to equilibrate by shaking at 200 rpm in a C24KC Refrigerated Incubator shaker for 0.5, 1, 3, 6, 9, 12, and 24 h at three reaction temperatures (15, 25, and 35°C). After each reaction time, 10-mL aliquots were taken and centrifuged for 30 min at 10,000 rpm in an IEC CL31R multispeed centrifuge (Thermo Electron Corp., Waltham, MA, USA). The reaction temperatures were maintained during centrifugation. Immediately after centrifuging, the samples were passed through $0.45 \mu\text{m}$ cellulose Nitrate membrane filters by vacuum filtration. Phosphorus concentrations in the filtrates were measured using a Vista inductively coupled plasma atomic emission spectrometer (Varian Inc., Palo Alto, CA, USA). Phosphorus sorption was calculated as the difference between the initial solution P concentration and the solution P concentration after reaction. Solution pH was measured with a Fisher Accumet AB 15 pH meter (Fisher Scientific, Hampton, NH, USA).

Statistical Analysis

A comparison, using PROC NLIN in SAS 9.4 (SAS Institute, 2013), of pseudo-first-order and pseudo-second-order kinetic models, which are commonly used in studies of P sorption by Fe oxides (Ainsworth and Sumner, 1985; Cui et al., 2011), indicated that the pseudo-first order model provided a better fit to our data. The pseudo-first order model is as follows:

$$q_t = q_e(1 - e^{-kt}) \quad [1]$$

where q_t is the sorption capacity (mg g^{-1}) at time t (h), q_e is the sorption capacity at equilibrium (mg g^{-1}), and k is the pseudo-first order rate constant (h^{-1}). Treatment differences in parameters were compared using 95% confidence intervals of the parameters.

The activation energy of P sorption (E_a , kJ mol^{-1}) was estimated by the Arrhenius equation using PROC NLIN:

$$k = A_e^{(-E_a/RT)} \quad [2]$$

where A is the frequency or pre-exponential factor (h^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K).

An ANOVA was performed on cumulative P sorption data at 24 h (which were normally distributed) using PROC MIXED in SAS 9.4, and the means were compared using the Tukey-Kramer mean comparison procedure.

RESULTS AND DISCUSSION

Biochar Characterization

Initial chemical properties (measured by a commercial laboratory) of the biochar used in this experiment are presented in Table 1. The concentrations of P, Ca, and Mg are similar to those reported for wood biochars in other studies (Atkinson et al., 2010; Zhao et al., 2013). Sorption results from the set of blanks consisting of the background solution with biochar but no oxides showed that the biochar P remained sorbed (i.e., did not go into solution) after 24 h of reaction (data not presented).

Phosphorus Sorption Kinetics

The sorption of P by Fe oxides was adequately described by the pseudo-first-order kinetic model. Phosphate was rapidly sorbed by the oxides within 2 h; this was followed by a slower and constant sorption pattern (Fig. 2). This sorption pattern has been reported in other studies (Luengo et al., 2007; Jaisi et al., 2010; Cui et al., 2011). Strauss et al. (1997) proposed that P is initially sorbed onto charged external surfaces of goethite during the period of fast P sorption and then diffuses into the particle, where slow and constant sorption takes place. Phosphorus precipitation on goethite was also proposed as a mechanism during the slow P sorption phase (Martin et al., 1988). As temperature increased, rate constants (k) increased from 3.8 to 7.7 h⁻¹ in the unamended goethite and from 2.8 h⁻¹ to 5.1 h⁻¹ in the biochar-amended goethite, indicating that P sorption by goethite is favored by the increasing temperature and thus is endothermic. The increase in the sorption rate constant and the sorption capacity with increasing temperature has previously been reported for iron oxides (Mezenner and Bensmaili, 2009; Luengo et al., 2007).

For Al- substituted goethite, in contrast, k decreased with increasing temperature from 1.8 h^{-1} to 0.8 h^{-1} in the absence of biochar and from 1.2 to 0.7 h^{-1} when biochar was added, indicating an exothermic reaction. However, k did not differ significantly among temperatures, between oxide types and between the two biochar rates.

Activation Energy (E_a)

The E_a for sorption of P by goethite was positive (1.53 kJ mol^{-1} with biochar added and 11.3 kJ mol^{-1} without biochar), which is consistent with the observed increase in the first order rate constant (k) as the temperature increased from 15 to 35°C . By contrast, E_a for P sorption by Al-goethite was negative ($-9.59 \text{ kJ mol}^{-1}$ with biochar added and $-29.3 \text{ kJ mol}^{-1}$ without biochar), which is consistent with the reduction in k as the temperature increased to 35°C . Averaged across temperatures and regardless of oxide type, E_a did not differ significantly between the 0 and the 40 g kg^{-1} biochar rates. The low magnitude of the E_a ($< \pm 42 \text{ kJ mol}^{-1}$) (Sparks 1989) obtained in this experiment is consistent with those reported in other studies for P sorption on Fe and Al oxides and hydroxides (Kuo and Lotse, 1973; Liu and Huang, 2000; Luengo et al., 2007). Low activation energies may indicate that P sorption is a diffusion-controlled process, occurring by means of physical sorption rather than chemisorption (Sparks 1989).

Cumulative Phosphorus Sorption

Biochar rate effect on cumulative P sorption varied with oxide type and temperature, as indicated by the significant biochar $\times$ oxide ($P = 0.02$) (Fig.3) and biochar $\times$ temperature ($P = <0.001$) (Fig.4) interactions (Table 3). The addition of biochar significantly increased the amount of P adsorbed by both oxides after 24 h of reaction. In the presence of biochar, Al-goethite adsorbed significantly more P than goethite. The observed increase in P sorption with biochar

addition is consistent with results from previous studies, which also showed greater sorption with the incorporation of biochar (Novak et al., 2009; Parvage et al., 2013; Xu et al., 2014). The sorption capacity of biochar arises from its high specific surface area and microporosity (Kookana et al., 2011; Zhao et al., 2017). Also, the positive charge of biochar may provide additional P sorption to that by the oxides (Lawrinenko and Laird, 2015). Even with a net negative surface charge, biochar may still have the potential to sorb P by other mechanisms that are not fully understood (Lehmann, 2007). It is also possible that some of the dissolved P is precipitated as phosphates of Ca and Mg (Novak et al., 2009). Although the levels of Ca (200 mg kg⁻¹) and Mg (20 mg kg⁻¹) in the biochar tested were probably low to make a significant impact on the solution concentrations of these elements (Atkinson et al., 2010).

Phosphorus sorption increased as temperature increased from 15 °C to 25 °C and the increase in sorption was statistically significant for the no biochar control treatment, indicating an acceleration in sorption with the increase in temperature. However, P sorption decreased when temperature increased from 25°C to 35°C in treatments with and without biochar (Fig 4). A similar temperature effect on P sorption was observed by Sheppard and Racz (1984), who reported a decrease in the amount of applied P extracted with an increase in incubation temperature from 10 °C to 25 °C, indicating an increase in sorption with the increase in temperature. A further increase in the incubation temperature in their study increased the P extractability, hence reduced the sorption, indicating endothermic desorption reactions. Similarly, Barrow and Shaw (1975) reported P desorption to be an endothermic reaction.

The kinetic data from this study provide some insights into the effect of temperature on P adsorption and indicate that biochar application can increase P sorption in soils containing Fe

and Al oxides. However, importantly, the low activation energies measured indicate that P is not strongly sorbed and may still be available to plants. Further studies with soils and various biochars are needed before field level P and biochar management strategies can be devised.

Conclusion

Overall, biochar application enhanced cumulative P sorption by both oxides, and the increase in sorption was greater for Al-goethite. Increased P sorption may minimize the off-site migration of bioavailable forms of P. Averaged across oxides, biochar application increased cumulative P sorption at the lowest temperature tested (15°C) but not at higher temperatures. Regardless of biochar rate, cumulative P sorption decreased significantly at 35°C relative to the two lower temperatures. Phosphorus sorption by biochar-amended oxides was associated with a low activation energy (E_a), indicating that the sorbed P in soils containing goethite and Al-goethite could still become available to plants.

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Table 1. Selected chemical properties of the biochar.

Ca [†]	Mg	K	Na	CEC	pH	N [‡]	C	P	S
mg kg ⁻¹				cmol _c kg ⁻¹		g kg ⁻¹		mg kg ⁻¹	
200	20	96	81	1.8	8.6	0.27	427	61	28

[†]Exchangeable cation concentrations in biochar; [‡] total C, N, P and S concentrations in biochar

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Table 2. Results of X-ray microanalysis of goethite and aluminum substituted goethite (Al-goethite).

Element	Goethite	Al-goethite
	%	%
Iron	71.8	73.5
Oxygen	26.9	23.5
Aluminum	0.69	2.96
Potassium	0.53	-

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Table 3. Least square mean cumulative phosphorus sorption as affected by biochar, oxide, and temperature after 24 h of reaction

Treatment	Cumulative P Sorption mg g ⁻¹
Biochar	
0	1.87 (0.08) [†]
40 g kg ⁻¹	2.26 (0.08)
Oxide	
Goethite	1.87 (0.09)
Al-goethite	2.27 (0.09)
Temperature	
15 C	2.19 (0.13)
25 C	2.83 (0.13)
35 C	1.18 (0.13)
	P value
Biochar	<0.001
Oxide	0.01
Temperature	0.0003
Biochar × Oxide	0.02
Biochar × Temperature	<0.001
Biochar × Oxide × Temperature	0.39

[†]Mean separation letters are not applied because the interactions are significant. The significant interactions are plotted in Fig. 3 and Fig. 4. Values in parenthesis are the standard error of mean.

Figure Captions

Fig. 1. Results of XRD analysis for Al-goethite (A) and goethite (B).

Fig. 2. Pseudo-first-order sorption kinetics of phosphorus by goethite and Al-goethite as affected by biochar application and temperature. Rate constants (k , h^{-1}) are presented for each temperature in the legend. RMSE, root mean square error.

Fig. 3. Differences in the amount of sorbed P after 24 h of reaction time for goethite and Al-substituted goethite, with and without biochar, averaged across temperature.

Fig. 4. Differences in the amount of sorbed P after 24 h of reaction time at 15°C, 25°C, and 35°C, with and without biochar.

279x361mm (300 x 300 DPI)