



Almond and walnut shell-derived biochars affect sorption-desorption, fractionation, and release of phosphorus in two different soils

Narges Hemati Matin ^{a,***}, Mohsen Jalali ^a, Vasileios Antoniadis ^b, Sabry M. Shaheen ^{c,d,**}, Jianxu Wang ^{e,c}, Tao Zhang ^{f,g}, Hailong Wang ^{h,i}, Jörg Rinklebe ^{c,j,*}

^a Department of Soil Science, College of Agriculture, Bu-Ali Sina University, Hamadan, Iran

^b University of Thessaly, Department of Agriculture Crop Production and Rural Environment, Volos, Greece

^c University of Wuppertal, School of Architecture and Civil Engineering, Institute of Foundation Engineering, Water- and Waste-Management, Laboratory of Soil- and Groundwater-Management, Pauluskirchstraße 7, 42285, Wuppertal, Germany

^d University of Kafrelsheikh, Faculty of Agriculture, Department of Soil and Water Sciences, 33516, Kafr El-Sheikh, Egypt

^e State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 550082, Guiyang, PR China

^f Beijing Key Laboratory of Farmland Soil Pollution Prevention and Remediation, Key Laboratory of Plant-Soil Interactions of Ministry of Education, Biomass Engineering Center, College of Resources and Environmental Sciences, China Agricultural University, Beijing, 100193, China

^g National Institute for Green Agriculture Development, China Agricultural University, Beijing, 100193, China

^h Key Laboratory of Soil Contamination Bioremediation of Zhejiang Province, Zhejiang A & F University, Hangzhou, Zhejiang, 311300, China

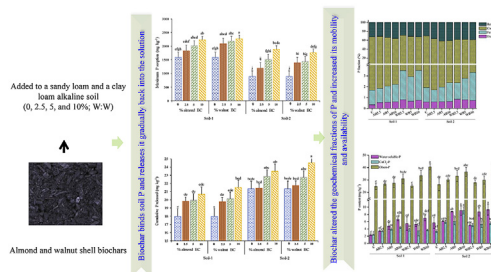
ⁱ School of Environment and Chemical Engineering, Foshan University, Foshan, Guangdong 528000, China

^j Department of Environment, Energy and Geoinformatics, Sejong University, 98 Gunja-Dong, Seoul, Republic of Korea

HIGHLIGHTS

- Almond and walnut shell biochars (BCs) increased P sorption in alkaline soils.
- Biochar released previously bound P gradually back into solution.
- Walnut BC-added soils sorbed more P than soils added with almond BC.
- Biochar-added P was distributed in the residual and exchangeable fractions.
- BC addition to soil resulted in increased water-soluble-, mobile-, and Olsen-P.

GRAPHICAL ABSTRACT



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ABSTRACT

Effective soil phosphorus (P) management requires higher level of knowledge concerning its sorption-desorption, fractionation, and release, as well as its interactions with soil amendments including biochar (BC). The purpose of this research was to investigate the influence of two different BCs, derived from almond and walnut shell, on P sorption-desorption and its redistribution among the geochemical fractions in two different soils. The BCs were applied to the soils in four doses (0, 2.5, 5, and 10% w/w) and the mixtures were incubated for one month. Phosphorus sorption increased due to the addition of BCs. Phosphorus sorption data fitted well the Freundlich isotherm and were simulated by the PHREEQC software. Biochar addition increased total P and the added P was mainly distributed in the exchangeable, Fe/Al–P and the residual fractions. Also, BC addition resulted in an increase in the water-soluble-,

* Corresponding author. University of Wuppertal, School of Architecture and Civil Engineering, Institute of Foundation Engineering, Water- and Waste-Management, Laboratory of Soil- and Groundwater-Management, Pauluskirchstraße 7, 42285, Wuppertal, Germany.

** Corresponding author. University of Wuppertal, School of Architecture and Civil Engineering, Institute of Foundation Engineering, Water- and Waste-Management, Laboratory of Soil- and Groundwater-Management, Pauluskirchstraße 7, 42285, Wuppertal, Germany.

*** Corresponding author.

E-mail addresses: n.hematimatin@agr.basu.ac.ir (N. Hemati Matin), jalali@basu.ac.ir (M. Jalali), antoniadis@uth.gr (V. Antoniadis), shaheen@uni-wuppertal.de (S.M. Shaheen), rinklebe@uni-wuppertal.de (J. Rinklebe).

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mobile-, and Olsen-P, making P more available for plant uptake. The kinetics data were well described by the simple Elovich, pseudo-second-order, and intra-particle diffusion equations. Walnut BC-added soils had higher P sorption capacity than those added with the almond BC. The results suggest that BC binds soil P and releases it gradually back into solution, making it thus available to plants; this renders the studied BCs promising materials for protecting P from being lost out of soil. Future research must be conducted over longer-term experiments that would study P dynamics in BC-added soils under real field conditions.

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1. Introduction

Phosphorus (P) is an essential macronutrient, required for plant nutrition; thus, P is considered one of the limiting factors for plant productivity (Han et al., 2018); P deficiency is a common phenomenon in agricultural soils worldwide. Despite the long-term application of phosphate fertilizers to increase crop yields, P availability is often low, due to the high affinity of phosphate for certain soil solid phases (McBeath et al., 2005; Kolahchi and Jalali, 2013). On the other hand, the accumulation of P leads to excessive P runoff caused by human activities, which in turn is a major contribution to eutrophication (Conley et al., 2009; Dodds et al., 2009; Zhang et al., 2012). Thus, efficient management practices are necessary in order to provide sufficient P to crops and avoid surface water contamination. Many factors influence P sorption by soil, including organic complexes (Debicka et al., 2015), Al and Fe oxides, clay minerals (Gérard, 2016), and calcite (Sø et al., 2011). Among these factors, organic matter (OM), as the main component in soils which is responsible for binding of anions, plays an important role in P sorption (Hunt et al., 2007; Debicka et al., 2015). However, application of OM has also been found to increase P availability in soils with high P retention ability (Agbenin and Igbokwe, 2006; Shaheen and Tsadilas, 2013). Biochar (BC), a carbon-rich material, is the final product of thermal degradation of organic biomass in the absence of oxygen (Lehmann, 2007; Lehman and Joseph, 2009; Shaheen et al., 2019). Previous studies have shown that BC application improved important soil physical and chemical properties, such as surface area, micro-porosity, and cation and anion exchange capacity (Soinne et al., 2014; El-Naggar et al., 2019a, El-Naggar et al., 2019b). As BC contains a large amount of P, its application enhances P availability and plant growth and can also increase P sorption or precipitation in soils (Wang et al., 2012; Xu et al., 2014). The BC effect on P cycle in soils has rarely been reported, especially concerning P sorption and desorption in different soils (Han et al., 2018). Despite the agreement of reports about the positive BC effects on P retention (Morales et al., 2013; Bruun et al., 2017), the role of BC on soil P sorption and availability is rather inconsistent and depends on the type and properties of BC and soils involved (Zhang et al., 2016; Dugdug et al., 2018; Hong and Lu, 2018; Kahura et al., 2018). Some studies have indicated that BC application to soil leads to an increase in P availability in soil (Jin et al., 2016; Sigua et al., 2016). Also, Bornø et al. (2018) found minimum additional P sorption capacity by soil resulting from BC amendment, due to limited electrostatic attraction and anion exchange capacity between some BCs and the negative-charge P ions (Vikrant et al., 2018; Purakayastha et al., 2019).

Some works (e.g., Shariatmadari et al., 2006; Shaheen et al., 2019) have pointed out that P desorption is highly affected by the common ions and can quite satisfactorily be explained using kinetics equations, but there is a scarcity of studies dealing with P desorption kinetics in BC-treated soils. Moreover, it is necessary to have more information on P chemical forms after BC interaction with soils; also, the mechanisms of the increase in P availability

must be elucidated. To this end, chemical fractionation of P in soil as affected by BC addition to soil provides an approach to quantify and characterize the forms and transformations of this nutrient in soil (Hedley and McLaughlin, 2005; Shaheen et al., 2007; Gerdelidani and Hosseini, 2017).

It has been reported that, with over 1.2 million metric tons in 2017/18, almond was the most highly produced nut tree. Also, walnut production was estimated at 871,850 metric tons, being the second world tree nut production. Iran contributed 4% of the world walnut production and 1% of the almond world production in (INC-2017/2018 Statistical Yearbook, 2018). Other studies have reported that almond shells account for 35–75% and walnut for ca. 67% of the total fruit weight (Martinez et al., 2003; Ebringerová et al., 2008; Pirayesh et al., 2012; Li et al., 2018). Thus, the effective use of waste nut shells is important in an effort to reduce the huge quantity of available solid waste and leads towards healthier environment. However, the effect of acidic BC such as those derived from almond and walnut shells on P fractionation and release in alkaline soils with different textures is not well-studied. Therefore, the aim of this work was to study the effects of almond and walnut shell-derived BC added to soils at various doses on sorption and desorption of P and its fractionation and release in a sandy loam and a clay loam. The novelty of this study lies in the fact that we elucidate all these aspects related to P behavior in alkaline soils amended with acidic BCs.

2. Materials and methods

2.1. Soil sampling and analyses

Two soils differing in their texture (soil-1 was a clay loam and soil-2 a sandy loam) were collected from the upper horizon (0–20 cm depth) of an agricultural area, Hamedan, Iran. The climate of the region is semiarid with a mean annual precipitation of 300 mm and mean annual temperature of 10.9 °C (Sabziparvar, 2003). The soils were a composite sample of 5 subsamples collected in each area. The soils were air-dried, ground to pass through a 2-mm sieve and stored until analysis. The soils were characterized for selected soil properties according to Rowell (1994): pH, EC, water-soluble Ca, Mg, Na, K, and P were measured in a 1:5 soil:distilled water (DW) ratio after 30 min of shaking. Total P was determined after ignition (550 °C, 1 h) and extraction with 1 N HCl (Andersen, 1976). Amorphous Al and Fe oxides were extracted as per Farmer et al. (1983). Iron was measured by atomic absorption spectrophotometry (AAS) and Al spectrophotometrically. Calcium carbonate (CaCO₃)-equivalent was determined with the acid neutralization method (Rowell, 1994). Soil chemical and physical characteristics are presented in Table 1.

2.2. Biochar production and characterization

The almond and walnut nut shell-BCs were produced by Nabertherm, Germany. The almond shell BC was produced with

Table 1
Characteristics of the studied soils and biochars.

Parameters	Unit	Soil-1	Soil-2	Almond BC	Walnut BC
pH		7.7 ± 0.04 [†]	7.9 ± 0.06 [†]	6.5 ± 0.2	5.6 ± 0.04
EC	μS cm ⁻¹	90 ± 2 [†]	200 ± 9 [†]	430 ± 20	560 ± 60
CaCO ₃	g kg ⁻¹	85.0 ± 11	56.0 ± 27	—	—
OM		14.0 ± 0.5	13.0 ± 0.8	—	—
Sand		211.0 ± 37	620.0 ± 21	—	—
Clay		322.0 ± 0.9	157.0 ± 5	—	—
Fe-ox	mg kg ⁻¹	418.8 ± 11.9	211.7 ± 7.6	19.6 ± 0.1	29.2 ± 0.06
Al-ox		74.4 ± 1.1	65.1 ± 0.08	9.8 ± 0.02	10.5 ± 0.01
Water soluble Ca		100.0 ± 3.2 [†]	23.7 ± 2.9 [†]	984.0 ± 4.7 ^{††}	848.0 ± 2.4 ^{††}
Water soluble Mg		20.0 ± 1.7 [†]	11.2 ± 1.0 [†]	200.0 ± 1.4 ^{††}	372.0 ± 1.8 ^{††}
Water soluble Na		91.4 ± 3.4 [†]	44.8 ± 4.9 [†]	320.0 ± 20.3 ^{††}	326.0 ± 23.4 ^{††}
Water soluble K		63.0 ± 9.5 [†]	2.4 ± 3.2 [†]	472.0 ± 32.4 ^{††}	578.0 ± 68.2 ^{††}
Water soluble P		2.7 ± 0.1 [†]	7.3 ± 0.02 [†]	124.0 ± 4.5 ^{††}	94.0 ± 10.2 ^{††}
Total P		693.1 ± 2.4	680.1 ± 7.3	3256.3 ± 37.1	3511.6 ± 55.9

EC: Electrical conductivity; OM: Organic matter; Fe-ox: Ferrous oxalate; Al-ox: Aluminum oxalate. [†]Solid: solution (H₂O) ratio = 1:5 for soils (Rowell, 1994) and ^{††}Solid: solution (H₂O) ratio = 1:20 (Sahin et al., 2017) for BCs.

pyrolysis at 500 °C and walnut shell BC with pyrolysis at 400 °C for 2 h. The two BCs were dried at 70 °C; subsequently they ground to pass through a 0.5-mm sieve. pH and EC of the BCs were measured in a 1:20 BC:DW ratio after 1 h of shaking (Sun et al., 2014). Water-soluble Ca, Mg, Na, K, and P in the BCs were measured in a 1:20 BC:DW ratio shaken overnight (Sahin et al., 2017). Total P in BCs was determined after digestion of 0.5 g of BC with concentrated HNO₃:HClO₄ (3:1) at 180 °C for 2 h (Sahin et al., 2017) (Table 1).

Fourier-transform infrared spectra (FTIR) of BCs were measured using 2 mg of ground sample in a KBr pellet by scanning from 400 to 4000 cm⁻¹, averaging 10 scans at 1 cm⁻¹- intervals with a resolution of 4 cm⁻¹. The crystallinity and phase identification of the sorbents were determined with XRD (Seifert 300 Diffractometer) with CuKα as the radiation source and Ni as the filter in the range 2θ = 0–70°. Scanning electron microscope (SEM) measurements were performed using a BEL Japan, Inc., to determine BC morphology. Surface area and average adsorption pore width of the selected fraction of adsorbents were determined with N₂ gas BET (Brunauer–Emmett–Teller) using a Micromeritics Chemisorption ASAP 2020 (Toles et al., 1997).

2.3. Incubation experiment

The two BCs were applied to the two soils in triplicates at rates equivalent to 0, 2.5, 5, and 10% w/w, and placed into 200 cm³-plastic containers. The range of rates of BC application was selected according to Xu et al. (2014) and Ippolito et al. (2016). Although such application rates are not practical at field scale, they are commonly used in similar experiments to clarify the advantages or drawbacks of higher levels to soil. The containers were covered with plastic film and incubated at constant temperature (25 °C). Soil water content was kept equal to the field capacity: weight loss due to evaporated water was adjusted by adding deionized water. Thirty days later, the soils were dried and stored until analysis. We used an incubation period of one month as suggested by Chintala et al. (2014), due to the similarity of their experimental settings to ours. We also decided that we should not have a longer incubation period, due to the possible risk of P mineralization and decreased P availability (as suggested by Azeez and Van Averbeke, 2010; and Yu et al., 2013).

2.4. Phosphorus sorption and desorption experiments

One gram of each sample of the incubated soils was shaken for 24 h with 20 mL of KH₂PO₄ containing 0, 20, 40, 60, 80, 100, and 200 mg P L⁻¹ with 10 mM KCl as a background electrolyte. Then,

samples were centrifuged for 5 min at 4000 rpm and filtered using a filter paper (Whatman 42). The P sorption data were fitted to Freundlich and Langmuir equations using the SigmaPlot 12.5 program, as follows:

$$\text{Freundlich } q = K_f C^{1/n}$$

$$\text{Langmuir } q = \frac{bK_l C}{1 + K_l C}$$

where q is the sorbed P content (mg kg⁻¹), C is the equilibrium solution concentration (mg L⁻¹), K_f (mg^{(n-1)/n} L^{1/n} kg⁻¹, reverting back to L kg⁻¹ if $n = 1$, i.e., in case of linearity) and n (unitless) are Freundlich constants, K_l is a Langmuir constant and b is the maximum adsorption capacity (mg kg⁻¹).

Desorption experiments were performed immediately after the completion of the sorption experiments. After removal of the supernatant and washing adsorbents three times with deionized water, 20 mL of 10 mM KCl were added to residual soils in the centrifuge tubes, the suspensions agitated for 24 h on a shaker at 3200 rpm, and then centrifuged and filtered. Phosphorus content was analyzed colorimetrically using the ascorbic acid/ammonium molybdenate method (Murphy and Riley, 1962).

2.5. Solubility, mobility, and availability of P

The untreated and BC-treated soils were extracted for their water-soluble, mobile, and available P content. Water-soluble-P (WS-P) was extracted using deionized water at a 1:5 soil:DW ratio and 30 min of shaking. Mobile P was extracted using 0.01 M CaCl₂ with a soil-to-solution ratio of 1:10 and 1 h of shaking (Kuo, 1996). Available P was extracted with 0.5 M NaHCO₃ (Olsen and Sommers, 1982; 1:20 soil:solution, shaking for 30 min). All suspensions were centrifuged for 5 min at 3200 rpm, filtered and P content in the filtrates was determined with the method mentioned above.

2.6. Phosphorus fractionation

The untreated and BC-treated soils were sequentially extracted for the different geochemical fractions of inorganic P based on the Hieltjes and Lijklema (1980) scheme. Briefly, 1 g of soils was weighed into a 50-mL polypropylene centrifuge tube and extracted sequentially with 40 mL 2 M KCl (Exch-P; represents exchangeable P), 0.1 M NaOH (Fe–Al–P; Fe–Al-bound P), 0.5 M HCl (Ca–P;

carbonate-bound P), and a 5:2 mixture of concentrated HNO₃ and HClO₄ (RES-P; residual P).

2.7. Kinetics analysis

One gram of BC-treated soils was shaken at 3200 rpm with 10 mL of 0.1 M KCl. Small suspension samples were withdrawn at certain time intervals (0.5, 1, 4, 8, 12, 24, 48, 72, and 96 h), filtered immediately and P in extracts was determined as above. Phosphorus kinetics data were fitted using the following equations:

$$\text{Elovich } q_e = a + blnt$$

$$\text{Pseudo - first - order } \log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t$$

$$\text{Pseudo - second - order } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

$$\text{Intra - particle diffusion } q_e = K_p t^{0.5} + C$$

where q_e is the concentration of released P (mg kg⁻¹); q_t is cumulative P released at time t ; t the time of release (h); a (mg kg⁻¹ h⁻¹) and b (mg kg⁻¹) are constants, with b being indicative of the P release rate; k_1 is pseudo-first-order rate constant (h⁻¹); k_2 is pseudo-second-order constant (mg kg⁻¹ h⁻¹); C and K_p are the intercept (mg kg⁻¹) and rate constant (mg kg⁻¹ h⁻¹) of intra-particle diffusion, respectively. The goodness of fitness of P release by these models was tested with the coefficients of determination (R^2) obtained by the regression of measured versus predicted values.

2.8. Geochemical modeling

A geochemical model, PHREEQC (version 2.18; Parkhurst and Appelo, 1999), was used to simulate the experimental data, improve understanding of P sorption behavior, and predict the trend of P sorption in the different treatments. The PHREEQC package is a geochemical calculation software based on the laws of equilibrium among solid, liquid, and gas phases. Equilibrium constants of surface complexation reactions between various soil components and P were obtained from previous studies (e.g., Devau et al., 2009) and surface complexation constants of BCs were obtained by fitting to the experimental data as shown in the Supplementary Material (Appendix A; Table S1). The best fit between measured and calculated data was evaluated by root mean square error (RMSE) and mean residual error (MRE) (Devau et al., 2011). The RMSE and MRE were normalized (NRMSE and NMRE) to the range of the observed data, or normalized to the mean of the observed data and to the mean residual error. These parameters are described as follows:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (X_{c,i} - X_{o,i})^2}{n}} \quad (1)$$

$$\text{MRE} = \frac{\sum_{i=1}^n (X_{c,i} - X_{o,i})}{n} \quad (2)$$

$$\text{NRMSE (or NMRE)} = \frac{\text{RMSE (or MRE)}}{X_o} \quad (3)$$

where $X_{o,i}$ is the measured P content; $X_{c,i}$ is the content calculated

by the model; X_o is the average of measured P content; and n is the number of samples.

2.9. Statistical analysis

The study was a two-factor experiment with completely randomized design; the two factors were soil and BC. Statistical analysis was conducted using the package SAS version 9.4. The ANOVA and Duncan's Studentized Range test were used to compare treatment means.

3. Results and discussion

3.1. Basic characterization of the studied soils and biochars

The soils were weakly alkaline with pH values of 7.7 for soil-1 and 7.9 for soil-2, while the BCs were acidic with pH values of 6.5 for the almond BC and 5.6 for the walnut BC (Table 1). The two soils were poor in their organic matter content (average of 13.5 g kg⁻¹). Soil-1 had a higher CaCO₃-equivalent content than soil-2. The two soils differed in their texture: soil-1 contained three times lower content of sand and two times higher content of clay than soil-2. Soil-1 also contained higher concentration of amorphous Fe and Al oxides and water-soluble Ca, Mg, K, and Na than those in soil-2. Such components, CaCO₃, clay and amorphous Fe and Al oxides alike, may react with P, leading to more efficient P sorption in soil-1 than soil-2. Total content of P was 693.1 in soil-1 and 680.1 mg kg⁻¹ in soil-2, while water-soluble P content in soil-2 was higher than that in soil-1. The BCs were richer in their content in total P than the soils, with 3256.3 for the almond BC and 3511.6 mg kg⁻¹ for the walnut BC (Table 1); this means that added BCs may improve P availability to plants if applied in agricultural soils.

3.2. Spectroscopic characterization of the biochars, soils, and biochar-treated soils

The spectral analysis of FTIR is important for identifying the BC functional groups (Yao et al., 2011). The peaks in the almond BC spectra were assigned to the following reactive groups: 1) broad O-H alcohol (3441.5 cm⁻¹); 2) medium C-H alkane (2891.3 cm⁻¹); 3) strong C=O (1702.8 cm⁻¹); 4) C=C cyclic alkene (1586.1 cm⁻¹); 5) medium O-H bending alcohol (1430.4 cm⁻¹); and 6) medium C-O (1056.9 cm⁻¹) (Fig. 1a). As for the walnut BC, the peak assignments in the spectra demonstrated many bands, including 1) broad O-H alcohol (3439.7 cm⁻¹); 2) medium C-H alkane (2883.0 cm⁻¹); 3) strong C=O (1702.8 cm⁻¹); 4) strong C=C cyclic alkene (1602.1 cm⁻¹); 5) O-H bending carboxylic acid (1424.9 cm⁻¹); and 6) weak C-O (1232.3 cm⁻¹).

For some studies reporting BC spectra produced at higher pyrolysis temperatures, the above described bands are assigned to different groups (Wang et al., 2015). Chen and Chen (2009) reported various bands in the spectra of orange peels BC due to -OH (at 3000-3690 cm⁻¹), and CH₂ (at 2927 and 1446 cm⁻¹), as well as aromatic C=C and C=O (at 1613 cm⁻¹). Some studies demonstrated that the peak assignments in the BC spectra were methyl C-H stretching compounds (2916 cm⁻¹), aromatic carbonyl/carboxyl C=O (1699 cm⁻¹), aromatic C=C and C=O (1595 cm⁻¹), as well as aliphatic C-O-C and alcohol -OH (1030 cm⁻¹) (Sun et al., 2011; Trazzi et al., 2016).

The FTIR spectra in both soils treated with 10% of almond and walnut BCs showed an increase in infrared peaks at the range of 1500-2000 cm⁻¹; they also exhibited fingerprint regions which were not evident in the untreated soils (Fig. 1b). For example, a new peak at ca. the 1590 cm⁻¹ C=C stretching appeared on the treated soil-2, which was not evident in the untreated soil-2, and this

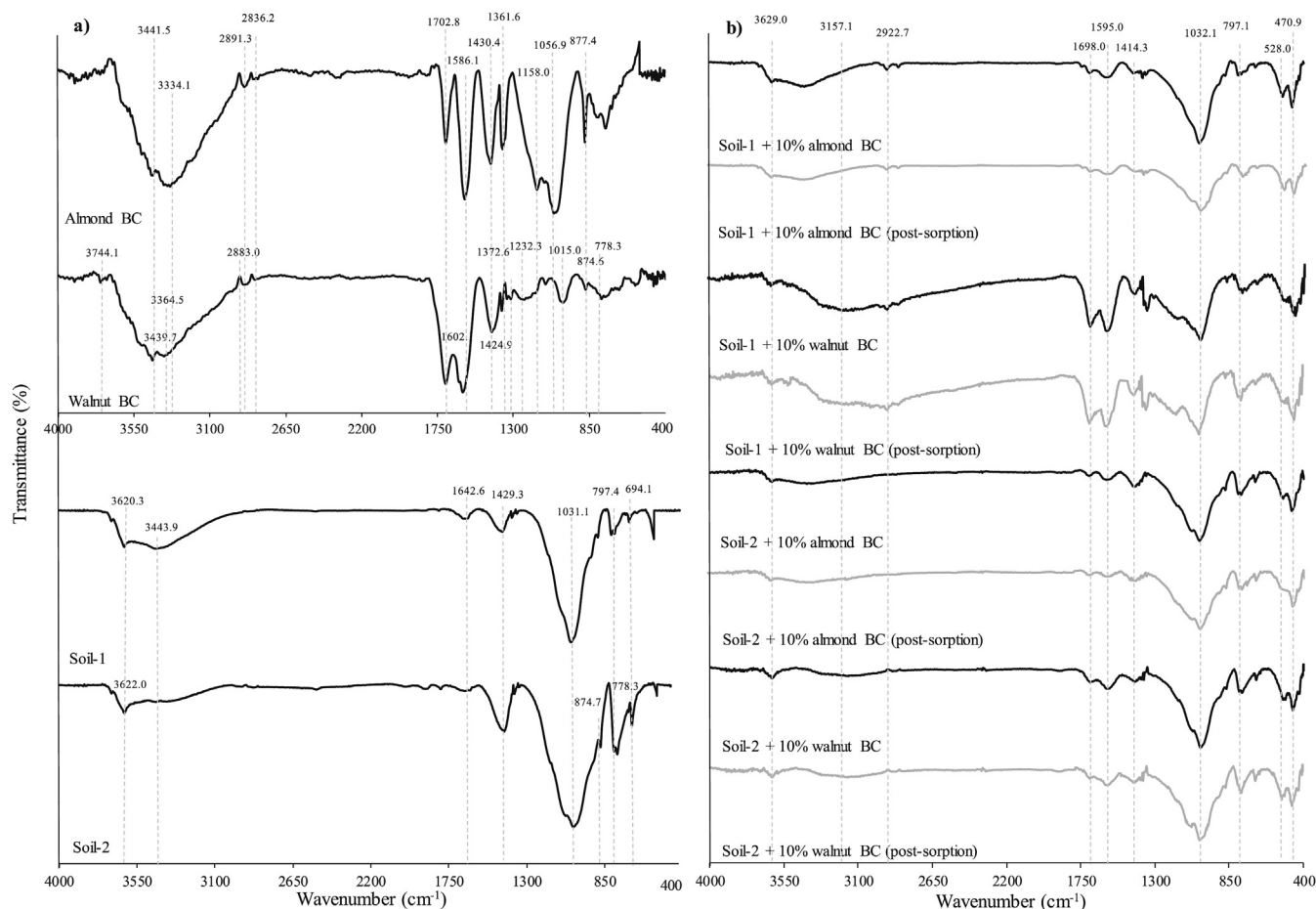


Fig. 1. Infrared spectroscopy of (a) the studied BCs, untreated soils, and (b) BC-treated soils (at 10% of added BC) before and after P sorption.

confirmed an increase in aromaticity during the incubation of soils with BCs. It has been shown in other similar works that some peaks shift after application of BC to soils because of the interaction between functional groups of BC and soil clay particles or due to a change in pH. For example, [Luo et al. \(2013\)](#) observed changes in the peak of the FTIR spectra in a soil treated with BC after incubation due to changes in soil pH. Also, [Parikh et al. \(2014\)](#) concluded that the presence of new peaks or shifts in wavenumbers of peaks is related to inner-sphere coordination. However, this new peak at ca. 1600 cm^{-1} , induced by monoaromatic alkanes, is rather short-lived due to expected rapid biodegradation ([Bushnaf et al., 2011](#)). The FTIR spectra of the 10% BCs-treated soils at the maximum added P concentration (200 mg L^{-1}) were obtained post-sorption in order to better study the effect of P sorption on the mixtures with the FTIR spectra ([Fig. 1b](#)). After P sorption, a decrease in some peak intensities was observed, while there were some other peaks that remained the same as those found before sorption. Similarly, other studies concluded that some strong FTIR spectra peaks of BCs were dropped post-sorption of P ([Zeng et al., 2013](#); [Trazzi et al., 2016](#)).

The SEM shows the state, surface and morphological properties of the studied solids. Sponge-, filamentary polygon- and skew polygon-like porous structures were observed in the particles of both BCs, as shown by the tracheid cells that were parallel to the axis ([Appendix A: Fig. S1](#) and [Fig. S2](#)). The pores were the result of released volatile gases from the BCs ([Appendix A: Fig. S1\(d\)](#) and [Fig. S2\(d\)](#)); thus, certain parts of BCs developed brittle skeletal structure with parallel slots that may be due to the decomposition

of some components occurring during BC pyrolysis ([Appendix A: Figs. S1\(c\) and S2\(b\)](#)). The walnut BC showed distinguishable honey-comb-like structures which may be due to the presence of tubular structures originally emanating from plant cells ([Nartey and Zhao, 2014](#)). The intensity of the BC XRD patterns did not show diffraction peaks ([Appendix A: Fig. S3](#)). There are two broad diffraction backgrounds corresponding to $2\theta = 10^\circ$ and $2\theta = 24^\circ$ in the spectra. Both XRD patterns revealed the amorphous nature of BCs. The BET results show that the activation of the walnut BC significantly increased their specific surface area ($107.3\text{ m}^2\text{ g}^{-1}$), which was 2.8 times higher than that of the almond BC ($38.7\text{ m}^2\text{ g}^{-1}$). The mean pore diameter was 6.1 nm for the almond BC, and 3.7 nm for the walnut BC.

3.3. Phosphorus sorption

Phosphorus sorption data were best described by the Freundlich isotherm, while the Langmuir model was not fitted well with the experimental data ([Table 2](#)). The Freundlich equation is widely recommended because of its accuracy in similar works; it has been repeatedly found to describe P sorption better than Langmuir ([Zhou and Li, 2001](#)). Sorption increased in the presence of the almond and walnut BCs in the two soils ([Fig. 2](#)), as also agreed by [Yao et al. \(2011\)](#) and [Zhang et al. \(2012\)](#). Sorbed P was enhanced by BC application as compared to the untreated soils. Soils treated with the walnut BC promoted higher P sorption than those amended with the almond BC mostly due to the presence of functional group

Table 2
Freundlich sorption isotherm parameters in untreated and BC-treated soils.

Soil	BC	BC Dosages %	Freundlich parameters				
			K_f L kg ⁻¹	n	R	SE	
1	Untreated	0	50.0	1.4	0.96	23.4	
		Almond	2.5	26.0	1.1	0.98	8.9
		5	18.0	1.0	0.99	3.0	
	Walnut	10	14.0	0.9	0.99	4.5	
		2.5	15.6	0.9	0.99	1.8	
		5	16.0	0.9	0.99	4.7	
2	Untreated	0	60.1	1.9	0.95	23.7	
		Almond	2.5	63.6	1.7	0.93	33.9
		5	14.8	1.1	0.98	7.2	
	Walnut	10	14.4	1.0	0.99	4.7	
		2.5	22.2	1.2	0.99	6.1	
		5	35.1	12.5	0.97	1.4	
			10	20.4	1.1	0.99	4.2

peaks around 1590 cm⁻¹ (C=C) and 1700 cm⁻¹ (C=O) (Fig. 1). As the rate of BC application increased, maximum P sorption increased in the two soils, but in the BC-treated soil-1 the increase in P sorption was greater than that in the BC-treated soil-2 (Fig. 3). Increased P sorption with BCs in the two soils may be the consequence of the fact that P was bound by oxyhydroxides borne in soils (Ippolito et al., 2016), and aliphatic and aromatic components borne in the BCs structures (Xu et al., 2014). The specific bonding of PO₄³⁻ with BCs is attributed to two types of hydrogen bonds: (i) bonds between phenolic end groups (C=O) of the BCs and protons of H₂PO₄⁻ and (ii) bonds between un-protonated oxygen of H₂PO₄⁻ and protons from surface-OH groups of the BCs (Sarkhot et al., 2014).

With the addition of both BCs, pH values decreased in the mixtures after incubation; the addition of 10% of almond and walnut BCs caused a decrease in pH compared to the untreated soil-1 (Appendix A; Table S2). Other studies also indicated that with the addition of acidic BCs, soil surface becomes more positively charged, causing a decrease in pH (Murphy and Stevens, 2010), thus increasing the formation of HPO₄²⁻ and promoting P sorption. Reduction of pH in our alkaline soils may also result in the precipitation of P with free Al and Fe oxides. Lindsay (2001) also found that pH significantly affected the sorption of P and that in acidic soils P was mainly fixed by high-energy sorption surfaces such as those found onto oxides and hydroxides of Fe and Al. However, in our soils the effect of acidic BCs on soil pH may over time be annihilated due to the presence of calcium carbonate, which tends to buffer soil acidity. In other similar studies, P sorption has not always been found to increase, as retention depends on the nature of added BC. Soinne et al. (2014) found that BC produced by a mixture of Norway spruce and Scots pine had a relatively low surface area and their addition to soil did not increase soil ability to sorb P. Nelson et al. (2011) reported even an increase in available P after BC addition due to the presence of low-molecular-weight organic acids (LMWOAs) and dissolution of P minerals; they also suggested inhibition of P sorption after soil addition of BC caused by LMWOAs. Novak et al. (2009) found that P availability and uptake increased with BC application (a consequence of reduced P retention by soil).

The P sorption at the maximum initial concentration of P of 200 mg L⁻¹ increased with BC addition (Fig. 3). There were significant differences between the two control soils and the 5% and 10% BCs-treated soils. Also, significant increase was observed in the 10% BCs-treated soils compared to the 2.5% BCs-treated soils in all cases, except for the sorption by the walnut-soil-1 mixture. For instance, in the high rate of added P (200 mg P L⁻¹), P sorbed in soil-1 treated

with 10% almond and walnut BCs were 2229.0 and 2281.0 mg kg⁻¹, respectively, while that in the untreated soil-1 was 1585.2 mg kg⁻¹ (Fig. 3).

Moreover, at maximum added P, the differences of P sorption were also significant between the two soils at control (higher in soil-1; Fig. 3). Also, P sorption was higher in soil-1 relative to soil-2 in all rates of BC addition, when same BC rates were compared. This can be explained by the fact that the higher clay content in soil-1 (322.0 g kg⁻¹) provides higher surface area available for sorption onto reactive groups at the edges of 1:1 and 2:1 minerals, and this seems to have affected the amount and energy of P sorption (Gérard, 2016). Soil-1 also had higher than soil-2 amount of Al and Fe oxides which exhibit high active P sorption capacity. This was agreed by Shaheen et al. (2009) and Antoniadis et al. (2016), who found that soils with higher clay and total "free" Al and Fe oxides increased P sorption. Indeed, it has been reported that P has high affinity to surfaces of various minerals and clays (Jalali, 2007; Huang and Zhang, 2011). Moreover, soil-2 had a lower CaCO₃ content (56.0 g kg⁻¹) than soil-1 (85.0 g kg⁻¹); therefore, P behavior in soil-1 seems to have been greatly influenced by its sorption onto, and precipitation with CaCO₃ surfaces (as also suggested by Jalali, 2007). Also, BCs can be a source of Ca and Mg; thus another possible mechanism for immobilization of P could be the flocculation of colloidal soil P with Ca and Mg ions and subsequently precipitation out of solution (Parvage et al., 2013).

In order to predict the effect of BCs on P sorption, simulation was performed using the PHREEQC program (version 2.18). Phosphorus sorption was considered to have taken place through complexation with Al and Fe hydroxides, calcium carbonate and BC reactive surface groups, as also discussed earlier. The equilibrium constants for P sorption onto the BCs were obtained by fitting the experimental data after trial-and-error cycles (Appendix A: Table S1). The simulation confirmed the experimental data of increased P sorption with BC addition in all treatments, and that soil-1 retained higher P concentrations than soil-2 (Fig. 2). Data also suggest that the mechanism of P retention by soils and BCs was mainly surface complexation. Domagalski and Johnson (2011) used PHREEQC and reported that P covered about 50% of the available sorption sites in soils at the highest added P. The functionality of this software was also agreed by Moharami and Jalali (2013), who showed that PHREEQC could adequately model P sorption by TiO₂, Al₂O₃ and Fe₃O₄ nanoparticles. In all treatments, the average NRMSE and NMRE values were lower than 0.67 and 0.53 mg kg⁻¹, respectively (Appendix A; Table S3). Such low values indicate low residual variance and demonstrate that PHREEQC is suitable for simulating P sorption in BC-treated soils. Also, PHREEQC confirmed that Fe-Al oxides were responsible for 24.4%–83.2% of the total soil P sorption, while calcite for 11.0%–75.2%.

3.4. Phosphorus desorption

The ratio of the desorbed P relative to the total sorbed can be used to indicate the degree of P release from the sorbate. The maximum P desorption for all treatments was achieved in the lowest initial P concentration (except for soil-2 treated with 5% of almond BC) and it decreased with increasing initial P concentrations (Fig. 4). This may be the consequence of the fact that BC addition increases aggregate stability and reduces detachment of colloidal material that could be beneficial for reducing particulate P losses from soils (Soinne et al., 2014). Total percentage of P desorption was higher for both treated soils with the walnut BC rather than the almond BC. There were no differences between the percentage desorbed from the untreated soils and BC-treated soils at high initial P concentrations (>80 mg L⁻¹) (Fig. 4); however, P

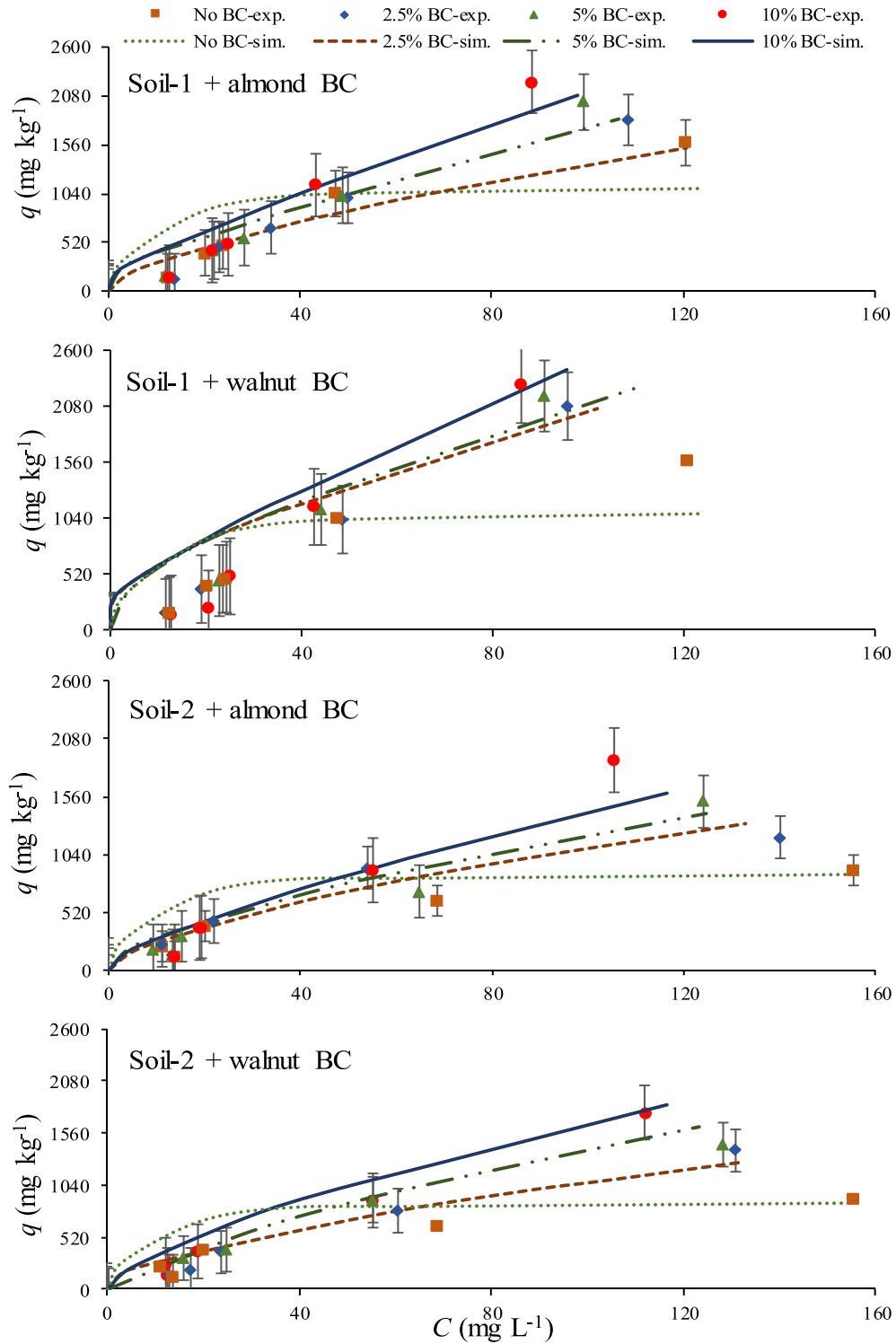


Fig. 2. Phosphorus sorption isotherms of the untreated and the BC-treated soils. Black diamonds represent experimental data and the lines correspond to the modeling results.

desorption percentage at low initial P concentrations for soil-1 was higher than that for soil-2. Han et al. (2018) reported that an increase in desorption of P with BC application could be due to the lower bonding energy (K_f) of P sorption (as evidenced here in Table 2). Other factors influencing P desorption from BC-treated soils may include desorption conditions, the gradient of P concentration, and the concentrations of various ions in solution (Cui et al., 2011).

3.5. Fractionation of P in the untreated and biochar-treated soils

Phosphorus distribution among its fractions is expressed as percentage of total content in Fig. 5 and as mg kg⁻¹ in the Supplementary Material (Appendix A; Table S4). The order of P fractions in the untreated and BCs-treated soils was as follows: Ca-P > RES-P > Fe-Al-P > Exch-P. About 56–68% of the sequentially extracted P was in the Ca-P fraction, which was 1.3- to 2.3-

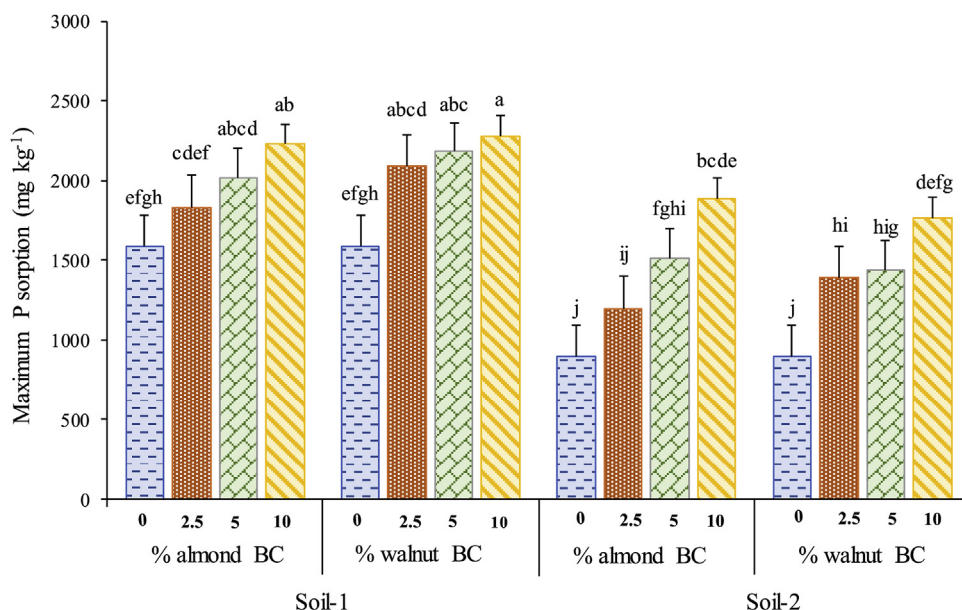


Fig. 3. Maximum P sorption (P sorption at 200 mg L⁻¹ of added P) in the untreated and BCs-treated soils. Values accompanied by different letters are significantly different within columns at the level of $P < 0.05$.

folds higher than the residual-P. This might be explained by the alkalinity and the relatively high carbonate content in both soils. The dominance of Ca-P in alkaline and carbonate-rich soils is in agreement with many other works (e.g., Shaheen et al., 2007; Halajnia et al., 2009; Jalali and Ranjbar, 2010; and Taghipour and Jalali, 2013).

Biochar addition increased total P from 680.1 mg kg⁻¹ to 1078.4 mg kg⁻¹ in soil-2 (Table S4), and caused a redistribution of P among its fractions (Fig. 5). The added P with BCs was mainly distributed in the exchangeable, Fe-Al-P, and residual-P. Biochars decreased the percentage of Ca-P (expressed as % of the total P), and increased the percentage of exchangeable-P, Fe-Al-P, and residual-P (Fig. 5). These results indicate that BCs shift P from the Ca-P fraction to the exchangeable, Fe-Al-P and residual-P fractions. The impact of the walnut BC on the exchangeable-P and Fe-Al-P was stronger than that of the almond BC, while the impact of the almond BC on the residual-P was stronger than that of the walnut BC (Fig. 5). The BC-induced increase of exchangeable-P (59–138%) and Fe-Al-P (12–103%) were higher in soil-1 than in soil-2, while the BC-induced decrease of Ca-P (13–17%) and the increase of residual-P (27–38%) were higher in soil-2 than in soil-1 (Fig. 5). The decreasing Ca-P percentage in the BC-treated soils as compared to the control might be explained by the associated decrease of soil pH (from 7.9 to 7.4) (Table S2), which may cause a release of P previously bound onto carbonates (Shaheen et al., 2009). On the other hand, the increased exchangeable-P in the BC-treated soils might be due to added surface area, increased porosity and the introduction of active sorption sites, i.e., the BC-borne aliphatic and aromatic components (El-Naggar et al., 2019a).

3.6. Solubility, mobility, and availability of P in the untreated and biochar-treated soils

The contents of water-soluble, mobile (CaCl₂-P), and available (Olsen-P) P are presented in Fig. 6. The Olsen-extracted P was expectedly higher than the mobile and water-soluble-P in both soils, with higher contents of the three indices found in soil-2 than in soil-1. Biochar addition increased significantly the water soluble (from 2.4 to 9.3 mg kg⁻¹), mobile (from 2.4 to 9.1 mg kg⁻¹), and

available P (from 24.7 to 40.5 mg kg⁻¹) relative to the control. Water-soluble-P and Olsen-P contents were higher in the soils amended with the walnut BC than those amended with the almond BC; that could be due to the higher P content recorded in the walnut BC (Griffin et al., 2017). In earlier works, it was shown that the application of BCs to soils could decrease P sorption capacity, and thus, increase P availability (Jiang et al., 2015; Qayyum et al., 2015; Chintala et al., 2014). The increase in availability of P may be attributed to P released from BCs irrespective of changes to surface properties (Chintala et al., 2014).

3.7. Kinetics of P release

The release of P was rapid, but with time the reaction became slower (Fig. 7). Cumulative P release from all treatments ranged between 18.0 mg kg⁻¹ (untreated soil-1) and 24.5 mg kg⁻¹ (10% of added walnut BC in soil-2) (Fig. 8). Differences among treatments of cumulative P release were not significant in most cases; however, P release had an increasing trend with added of BCs. For example, cumulatively released P in treated soil-2 with 2.5% of walnut BC was 21.8, at 5% it was 22.7, and at 10% it was 24.5 mg kg⁻¹. These findings are in agreement with those in the study of Liang et al. (2014), who observed that P release was higher at 5% of soil-added BC than that at 2.5%. During the 144 h of P release, only as low as about 3.2% of the total sorbed P was released, indicating that BCs could be used as a slow-P-release amendment when applied to soils.

When the two BCs within each soil were compared, there were no significant differences in cumulative P release: in soil-2 at 2.5% of the almond BC addition it was 21.4 (21.8 mg kg⁻¹ for the walnut BC) and at 10% it was 23.5 mg kg⁻¹ for the almond BC (24.5 for the walnut BC). On the other hand, when compared between the two soils, P release at the 5% of the almond BC-soil-1 treatment was significantly lower than that in soil-2; similar was the case with P released in the 10% added almond BC. The same occurred with P released in the 5% and 10% of the walnut BC additions (i.e., release in soil-1 was lower than in soil-2). For example, cumulative P release in soil-1 treated with 10% of almond and walnut BCs were 20.7 and 21.5 mg kg⁻¹, respectively, while the corresponding values in soil-2 treated with 10% almond and walnut BCs were 23.5 and

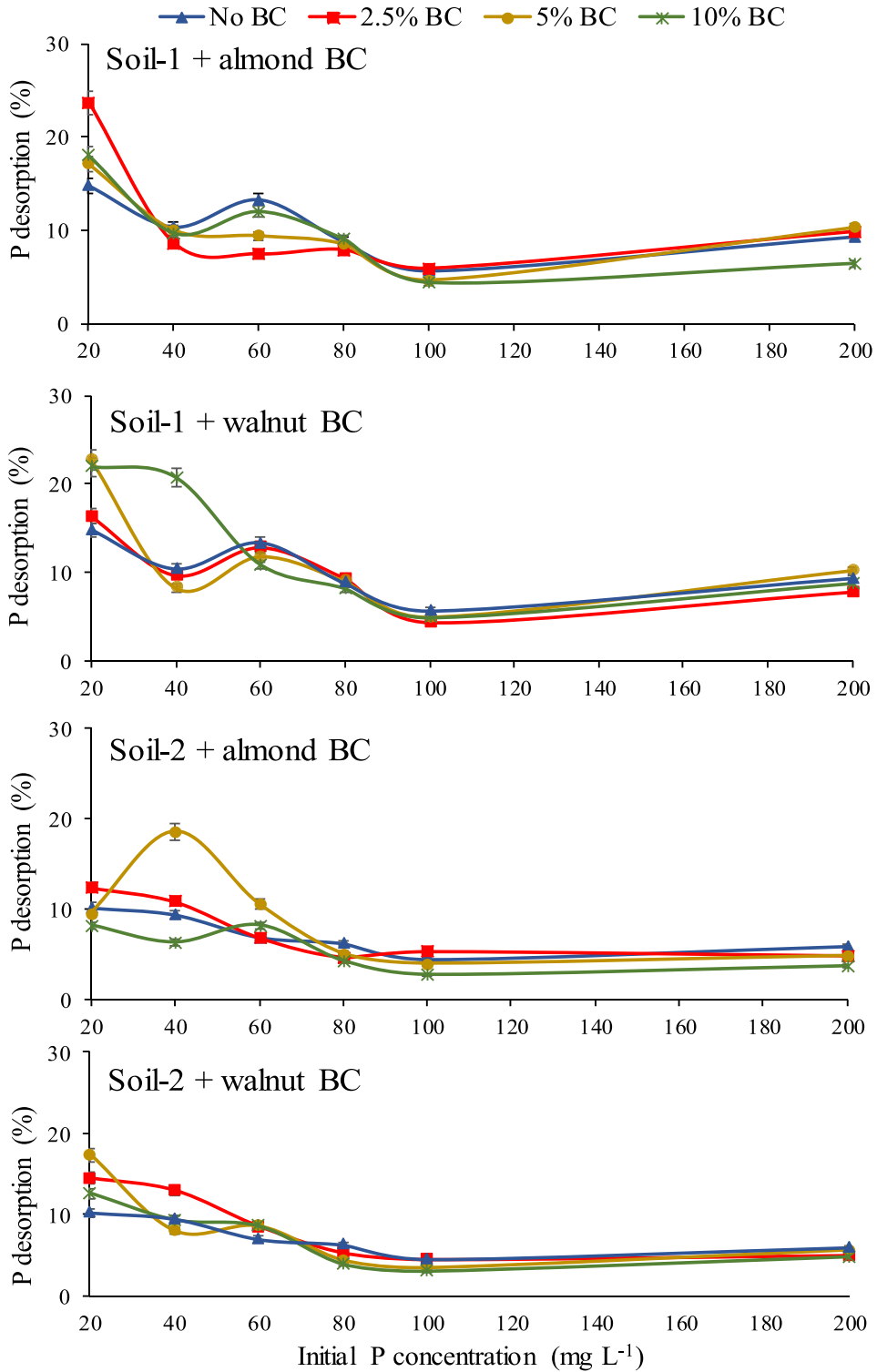


Fig. 4. Phosphorus desorption from the untreated and BCs-treated soils.

24.5 mg kg⁻¹, respectively.

In order to investigate the kinetics of P release, different kinetics models were used including the pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models (Table 3). Release kinetics was inadequately described by the pseudo-first-order model, as indicated by the fact that the experimental $q_{e,exp}$

values were different from the simulated $q_{e,cal}$ values. On the other hand, P release kinetics seems to be described well by the pseudo-second-order model, as exhibited in the similarity between observed ($q_{e,exp}$) and simulated values ($q_{e,cal}$) and the higher R^2 values compared to those of the pseudo-first-order model.

Also, P release kinetics was described well with the intra-

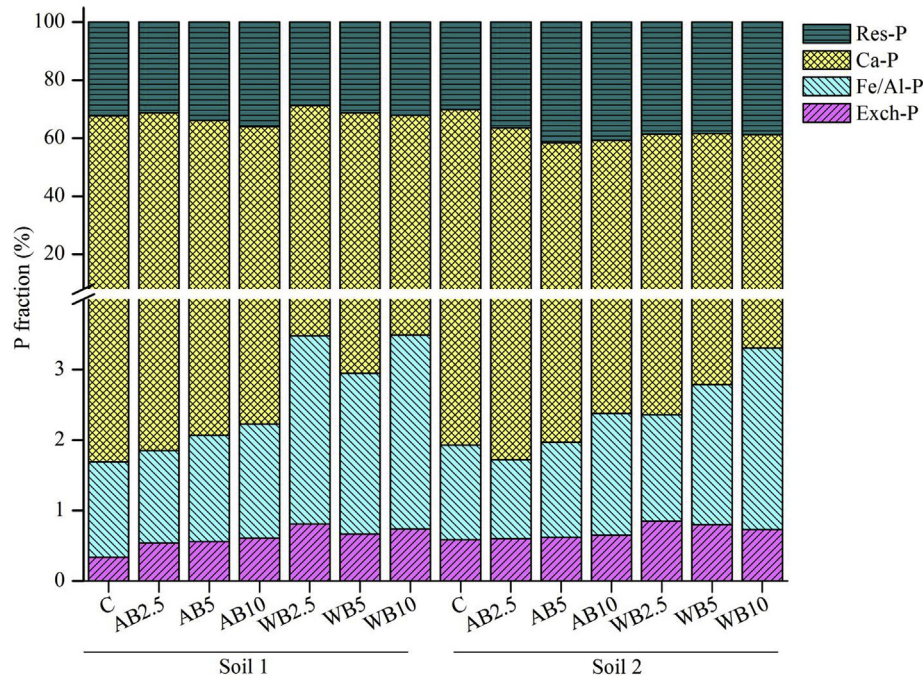


Fig. 5. Impact of BCs on the P fractions (expressed as percentage of the total P).

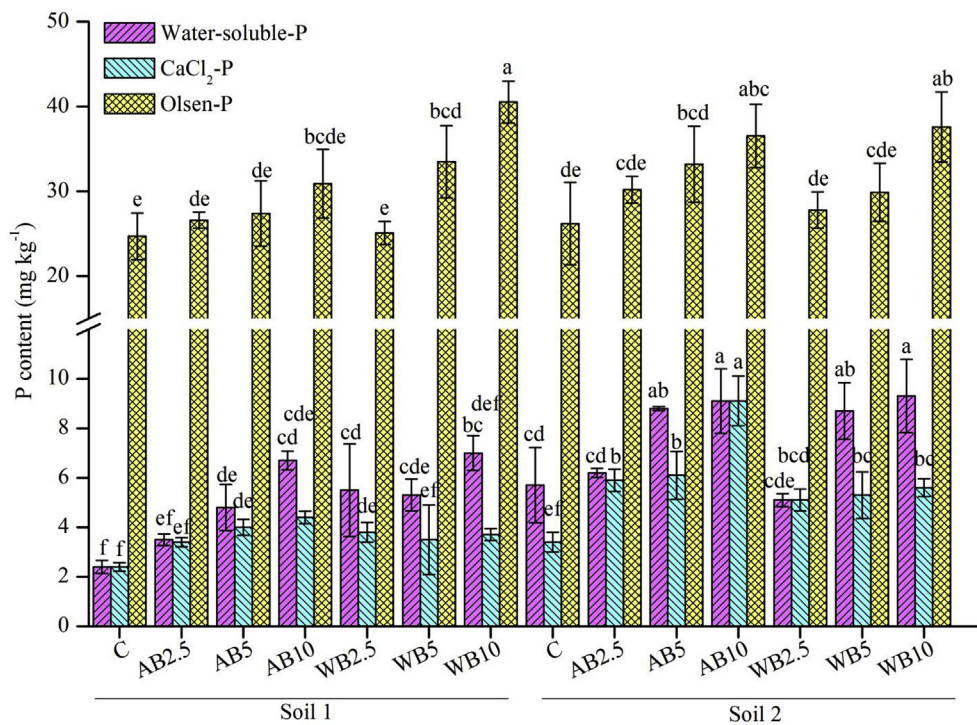


Fig. 6. Impact of BCs on the water soluble-, CaCl₂-, and Olsen-P in the soils.

particle diffusion model. The *C* values give information about the thickness of the boundary layer; i.e., the higher the intercept, the greater the boundary layer (Özcan and Özcan, 2004). In this study, *C* ranged from 1.8 to 4.5 mg kg⁻¹ and an increase was observed with added BCs in soil-2, while in soil-1 there was a decrease as BC rate increased. Data indicated that the P release process was influenced by two or more distinct steps. The first sharper portion may be

attributed to film diffusion. The second linear portion was the gradual slow release stage, where intra-particle diffusion is considered as a rate-limited factor (Chen et al., 2011). The close agreement between the calculated and measured P release for the treatments of both soils and of the two BCs by Elovich confirms that this model describes accurately the release of P. Also, the rate of release (*b* constant in the Elovich equation) increased with BC

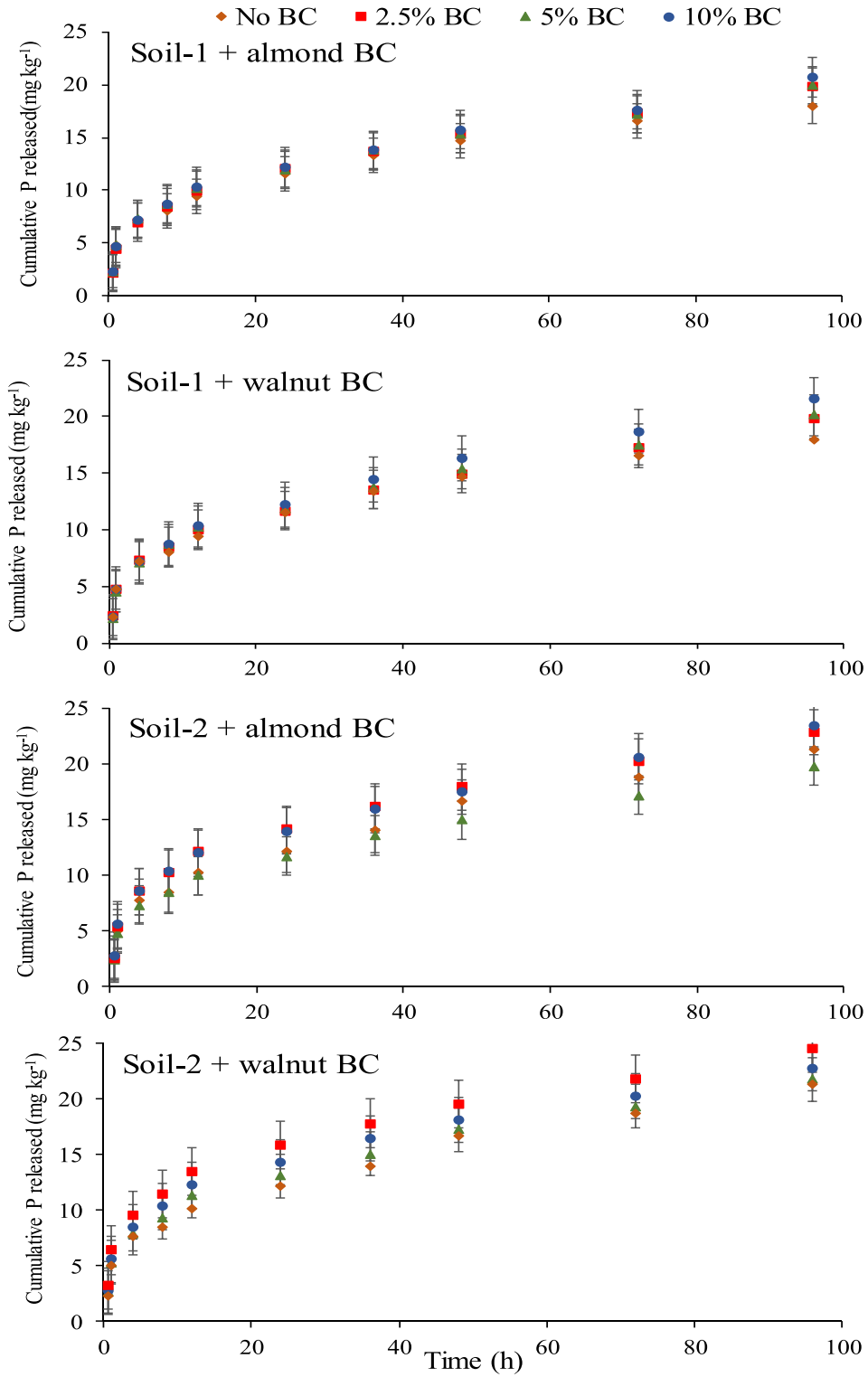


Fig. 7. Release kinetics of P from the untreated and BCs-treated soils.

addition. Such increased P release from BC-treated soils has an important implication for soil, owing to the fact of the sparingly available and widely variable water-soluble P under normal field conditions.

4. Conclusions

Sorption studies were conducted to establish the relationship between sorbed P and available P in order to evaluate the fate of P in soils. The BCs in this experiment had the ability to sorb P, which would have the implication of reducing P leaching from agricultural

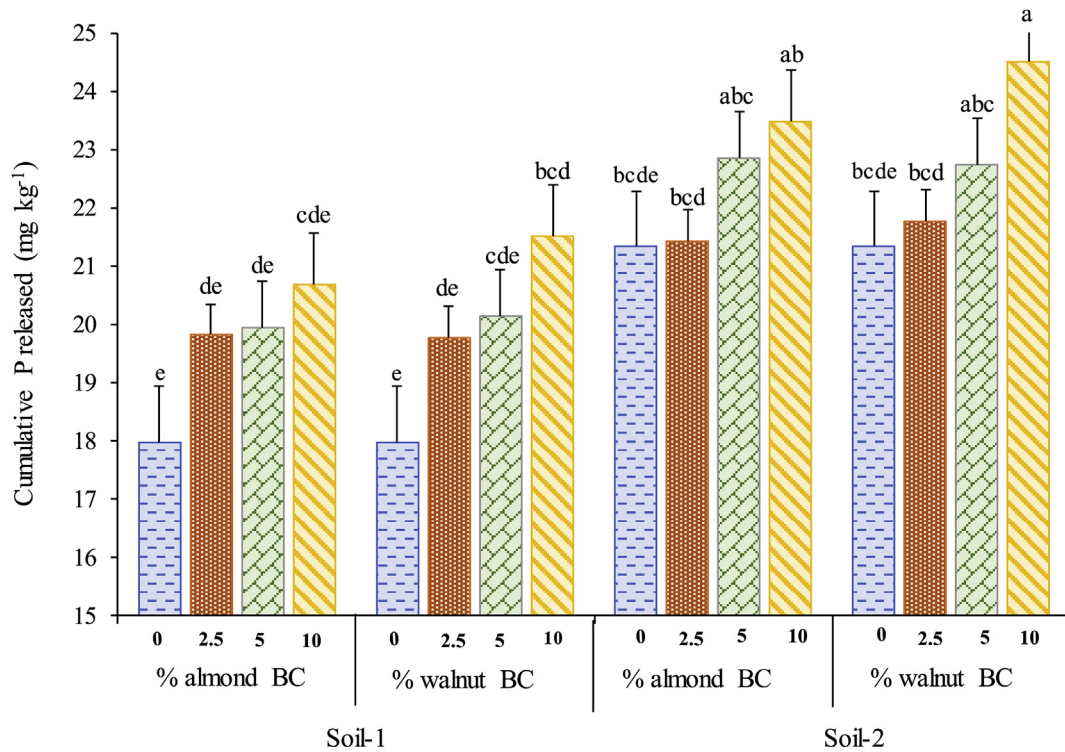


Fig. 8. Cumulative P release (mg kg^{-1}) from the untreated and BCs-treated soils. Values accompanied by different letters are significantly different within columns at the level of $P < 0.05$.

Table 3

Values of coefficients and parameters that describe P release kinetics in the studied soils.

Soil	BC	Biochar Dosages (%)	$q_{e, exp.}$ (mg kg^{-1})	Pseudo-first order			Elovich			Pseudo-second order				Intra-particle diffusion				
				R^2	$q_{e, cal}$ (mg kg^{-1})	k_1 (h^{-1})	R^2	a	b (mg kg^{-1})	$q_{e, cal}$ (mg kg^{-1})	R^2	$q_{e, cal}$ (mg kg^{-1})	k_2 ($\text{mg kg}^{-1} \text{h}^{-1}$)	R^2	C (mg kg^{-1})	Kp ($\text{mg kg}^{-1} \text{h}^{-1}$)		
1	Untreated	0	17.97	0.97	13.22	0.032	0.96	3.65	2.81	16.45	0.96	18.57	0.006	0.97	3.17	1.61		
		2.5	19.74	0.98	14.68	0.024	0.95	3.62	3.04	17.50	0.97	20.12	0.005	0.98	3.06	1.75		
		5	19.82	0.98	14.94	0.025	0.95	3.36	3.09	17.49	0.97	20.19	0.005	0.98	2.79	1.78		
		10	20.69	0.98	15.48	0.023	0.94	3.53	3.15	17.92	0.97	20.85	0.004	0.98	1.84	1.83		
	Walnut	2.5	19.78	0.98	14.74	0.024	0.95	3.60	2.99	17.27	0.97	20.00	0.005	0.98	3.01	1.73		
		5	20.14	0.98	15.17	0.025	0.95	3.45	3.12	17.67	0.97	20.45	0.005	0.98	2.87	1.80		
		10	21.51	0.99	16.68	0.025	0.94	3.43	3.33	18.61	0.96	21.98	0.004	0.99	2.69	1.94		
		2	Untreated	0	21.32	0.98	16.61	0.026	0.93	3.55	3.28	18.53	0.97	21.91	0.004	0.98	2.81	1.92
				2.5	21.43	0.98	15.80	0.025	0.96	4.00	3.28	18.99	0.97	21.72	0.005	0.97	3.43	1.89
			Almond	5	22.84	0.98	16.88	0.026	0.96	4.18	3.57	20.48	0.98	23.27	0.004	0.97	3.62	2.04
10	23.48			0.91	17.56	0.024	0.95	4.28	3.55	20.51	0.97	23.74	0.004	0.98	3.60	2.05		
Walnut	2.5	21.78	0.98	16.41	0.026	0.95	3.99	3.37	19.35	0.97	22.28	0.004	0.98	3.34	1.94			
	5	22.74	0.98	16.65	0.027	0.96	4.36	3.55	20.55	0.98	23.20	0.005	0.97	3.80	2.02			
		10	24.51	0.98	17.45	0.026	0.97	5.10	3.75	22.22	0.98	24.86	0.005	0.97	4.54	2.13		

$Q_{e,exp.}$: experimented amount of P released (mg kg^{-1}); $q_{e,cal.}$: calculated amounts of P released (mg kg^{-1}) with kinetics equations.

soils. Our findings suggest that added BCs may improve the availability of recently added P and even reduce the need for P fertilization in BC-treated soils. Also, this study showed that BCs have the potential to increase functional groups in soils, which may be beneficial to reduce the potential loss from soils of applied P. The addition of BC to soils, as opposed to the application of P fertilizers, may not only increase the amount of available P, but may also provide long-lasting P source to soils and, consequently, reduce the P losses to surface water bodies. For a better understanding of P behavior in BC-treated soils, such findings need to be confirmed by long-term experiments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.124888>.

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