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Mechanism of orthophosphate (PO$_4$-P) adsorption onto different biochars

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**Abstract**

The adsorption mechanisms of phosphate (PO$_4$-P) onto cocoa pod husk (CP), corn cob (CC), rice husk (RH) and palm kernel shell (PK) biochar pyrolyzed at 300 °C and 650 °C were investigated. A series of batch experiments were undertaken to assess the effects of contact time and pH. Results show that PO$_4$-P adsorption equilibria for the biochar types was within 6–15 h, being rapid in the 300 °C-biochar types. The equilibrium pH for maximum PO$_4$-P adsorption varied among biochar types, ranging from of 2.6 to 4.8 and increasing with decreasing PO$_4$-P adsorption. Pseudo-second-order and Elovich models explained the adsorption data well indicating a chemisorption process on heterogeneous biochar surface. PO$_4$-P adsorption was controlled initially by intraparticle diffusion and subsequently by chemisorption. Per the properties of the biochars (FTIR and elemental composition) and pH (equilibrium pH and ΔpH), PO$_4$-P was adsorbed through electrostatic attraction, surface precipitation and ligand exchange, and the relative importance of these processes differed among the biochar types. Biochar types (PK300, PK650, CP300, CP650, RH650 and CC650) that adsorbed PO$_4$-P through surface precipitation and ligand exchange reactions can be used to remove PO$_4$-P from wastewater since PO$_4$-P is strongly adsorbed, controlling PO$_4$-P enrichment of water bodies.

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1. Introduction

Adsorption of phosphate (PO$_4$-P) by organic material is of relevance in controlling the transport, mobility and enrichment of PO$_4$-P in aquatic environment. Although PO$_4$-P is an essential nutrient for the growth of plants and other living organisms, it can also serve as an environmental pollutant (Dodds et al., 2008; Almeelbi and Bezbaruah, 2012). About 0.02 mg L$^{-1}$ of dissolved PO$_4$-P in water bodies is considered to have potential risk to the proliferation of algal growth (USEPA, 1995). The increased PO$_4$-P in water bodies as a result of inappropriate and frequent discharge of waste water stimulates excessive growth of phytoplankton and algae which in turn decrease the quality of drinking water (Dodds et al., 2008). Thus, in order to reduce the negative effects of overloading water bodies with PO$_4$-P, it is necessary to assess various strategies and to evaluate the PO$_4$-P removal effectiveness of adsorbents that could be exploited for use as waste water cleansing agents of PO$_4$-P ions prior to wastewater discharge into natural water bodies (Biswas et al., 2008).
To treat PO₄-P contaminated water, a number of technological approaches have been deployed such as electrodialysis, reverse osmosis, chemical precipitation, membrane technologies, biosorption and ion exchange (Demirbas, 2008). The less expensive, technologically and environmentally friendly among the aforementioned methods is biosorption technique, and biochar is a common biosorbent. Biochar is a carbon-rich, fine grained, and porous material. It is usually produced by thermal decomposition of biomass under limited oxygen conditions at temperatures <850 °C (Demirbas, 2008). It has gained a lot of attention in recent times not only for its role in soil fertility improvement and carbon sequestration but also as a low-cost adsorbent for wastewater treatment (Yao et al., 2012; Zhang et al., 2016). Reports have indicated that biochar has a strong ability to remove chemical contaminants in water including PO₄-P, organic contaminants and heavy metals (Kasozi et al., 2010; Yao et al. 2013; Zhang et al., 2016). Due to its highly-porous structure, mineral contents (e.g. CaCO₃, Fe and Al) and functional groups (e.g. phenolic, carboxylic and amino groups), biochar has a high affinity for PO₄-P (Li et al., 2017). However, the adsorptive properties of biochar depends largely on the feedstock and pyrolysis temperature (Zhao et al., 2013).

Adsorption kinetics expresses the time-dependent removal of adsorbate by an adsorbent in an aqueous solution and its application is relevant for elucidating adsorption mechanism (Wahab et al., 2011; Jung et al., 2015; Zhang et al., 2015). Using chemical adsorption kinetic models (e.g. pseudo-first-order, pseudo-second-order, Elovich and Johnson–Mehl–Avrami), the mechanism of PO₄-P adsorption by biochar has been reported to be due to chemisorption (Yao et al., 2011; Wahab et al., 2011; Jung et al., 2015; Zhang et al., 2016). However, most of these studies did not focus on biochar at different pyrolysis temperatures. It is, therefore, important to clarify the magnitude of the chemical interactions between PO₄-P and biochar at different pyrolysis temperatures as a function of time and pH in a chemical system. In the present study, PO₄-P adsorption dynamics on four biochar types at two pyrolysis temperatures were investigated. The objectives of the study were to (1) determine contact time and pH effect on PO₄-P adsorption and (2) to elucidate possible mechanism for PO₄-P adsorption onto biochar.

2. Materials and methods

2.1. Biochar

The four biochar types produced at two different pyrolysis temperatures (300 °C and 650 °C) from cocoa pod husk (CP) (Theobroma cacao), corn cob (CC) (Zea mays), rice husk (RH) (Oryza sativa) and palm kernel shell (PK) (Elaeis guineensis) were obtained from the Soil Research Institute of the Council for Scientific and Industrial Research (CSIR), Ghana. All biochars were finely ground to <1 mm using a mortar and pestle and stored in air-tight bags until characterization and kinetics studies. The CP, CC, RH and PK feedstocks pyrolyzed at 300 °C and 650 °C are herein after designated as CP300, CP650, CC300, CC650, RH300, RH650, PK300 and PK650, respectively. Detailed description of the biochar types used for the study are shown in Table 1. Briefly, the pH, total P, total C, the concentration of the base cations (Ca, Mg, K and Na) and heavy metals (Fe and Al) increased with increasing pyrolysis temperature with the exception of the of total N and cation exchange capacity (CEC) which decreased otherwise.

2.2. Fourier transform infrared (FTIR) analysis and Boehm titration

The functional groups on the biochar types were examined using photoacoustic spectroscopy (PAS)-FTIR. In short, the spectra were recorded using a Nicolet 6700 (Thermo Scientific, USA) spectrometer equipped with a PA-301 photoacoustic
The dominance of the total surface acid functional groups on the biochar types were in the order of CC (0.97–2.10 mmol surface acid functional groups (carboxylic, phenolic and lactonic groups) varied with feedstock and pyrolysistemperature. Results from the Boehm titration were used to further quantify the acid functional groups on the biochar types at the two temperature regimes (300 °C and 650 °C) (Table 1). Obviously, the surface acid functional groups (carboxylic, phenolic and lactonic groups) varied with feedstock and pyrolysistemperature. The dominance of the total surface acid functional groups on the biochar types were in the order of CC (0.97–2.10 mmol g⁻¹) > CP (0.94–2.12 mmol g⁻¹) > RH (0.60–2.04 mmol g⁻¹) > PK (0.80–1.82 mmol g⁻¹). Consistent with the results of the FTIR, the content of surface acid functional groups decreased with increasing pyrolysistemperature, indicating the transformation of aliphatic moieties into aromatic moieties (Chun et al., 2004). The results suggested that biochar types charred at 300 °C have larger amount of acid functional groups compared to when charred at 650 °C.

2.3. Kinetics analysis and pH effect on PO₄-P adsorption

Kinetics study was carried out to determine the equilibrium time of PO₄-P adsorption onto the biochar types. PO₄-P solution was prepared by dissolving potassium dihydrogen phosphate (KH₂PO₄) in 10 mM potassium chloride (KCl). The PO₄-P kinetics of each biochar were examined by mixing 0.5 g of biochar with 30 mL of 100 mg L⁻¹ PO₄-P solution in 50 mL centrifuge tubes. The tubes were shaken on an end-to-end shaker at 120 rpm for 24 h at room temperature (22 ± 0.5 °C). A tube was withdrawn after the shaking was done for 1, 3, 5, 9, 15 and 24 h. The suspension was then centrifuged (3500 rpm, 15 min) and the resulting supernatant was filtered through a 0.45 µm filter paper. The filtrate was analyzed for PO₄-P by the colorimetric molybdenum-blue method (John, 1970).

The effect of solution pH on PO₄-P adsorption onto biochars was studied in an initial pH range of 2.5, 3.5, 4.5, 5.5, 6.5, 7.5 and 8.5. The pH was adjusted using 4 M HCl or NaOH. The ratio of biochar to the initial solution PO₄-P concentration was the same as the kinetics experiment. Furthermore, for each pH, a blank (0.5 g biochar per 30 mL deionized water without PO₄-P solution) was also included. The centrifuge tubes were shaken on an end-to-end shaker at 120 rpm for 24 h at room temperature (22 ± 0.5 °C). The suspension was then centrifuged (3500 rpm, 15 min) and the resulting supernatant was filtered through a 0.45 µm filter paper. The filtrate was analyzed for PO₄-P by the colorimetric molybdenum-blue method (John, 1970) and equilibrium (final) pH was also measured. The initial aqueous PO₄-P concentration Cᵢ (mg L⁻¹) and the equilibrium PO₄-P concentration Cₑ (mg L⁻¹) were measured and the PO₄-P adsorbed (qᵢ) was computed from the mass balance equation (Eq. (1)):

\[ qᵢ = \frac{(Cᵢ - Cₑ)V}{M} \]

(1)

Here, V is the volume of the aqueous solution (L) and M is the dry weight in grams of biochar (adsorbent).

2.4. Statistical analysis

The coefficient of determination (R²), standard error and other statistics, as well as fitting all kinetics data were done using Origin Pro 8.5 and RStudio v.3.4.2. The standard errors of the fitted coefficients were within 95% confidence intervals. Error bars were used to represent standard errors of triple determinations.

3. Results and discussion

3.1. Biochar FTIR and Boehm titration

FTIR spectrum of CC, PK, CP and RH at 300 °C and 650 °C revealed the information about adsorption process (Fig. 1). The bands at 1720/1396, 3400 and 2925 cm⁻¹ prove the existence of carboxylic C(-COOH), phenolic O-H and aliphatic -CH₂ stretch, respectively (Chun et al., 2004; Bourke et al., 2007; Brewer et al., 2009). These vibrational bands were relatively intense at 300 °C-biochar types as compared to their counterparts. The decrease in peaks 3400 cm⁻¹, 1396 cm⁻¹ and 1720 cm⁻¹ at 650 °C suggests the decrease in acid functional groups at high pyrolysistemperature (Brewer et al., 2009). Usman et al. (2015) and Chun et al. (2004) also reported a decrease in –COOH groups (acid functional group) with increasing pyrolysistemperature and even disappearance at high temperature. A well-stretched band centered around 800 cm⁻¹ and 1100 cm⁻¹ correspond to silicates (Bourke et al., 2007). Another noticeable band was seen at 875 cm⁻¹, which is assigned carbonate (Brewer et al., 2009). Results from the Boehm titration were used to further quantify the acid functional groups on the biochar types at the two temperature regimes (300 °C and 650 °C) (Table 1). Obviously, the surface acid functional groups (carboxylic, phenolic and lactonic groups) varied with feedstock and pyrolysistemperature. The dominance of the total surface acid functional groups on the biochar types were in the order of CC (0.97–2.10 mmol g⁻¹) > CP (0.94–2.12 mmol g⁻¹) > RH (0.60–2.04 mmol g⁻¹) > PK (0.80–1.82 mmol g⁻¹). Consistent with the results of the FTIR, the content of surface acid functional groups decreased with increasing pyrolysistemperature, indicating the transformation of aliphatic moieties into aromatic moieties (Chun et al., 2004). The results suggested that biochar types charred at 300 °C have larger amount of acid functional groups compared to when charred at 650 °C.
Fig. 1. Photoacoustic spectroscopy-FTIR analysis of (a) corn cob biochar (CC) charred at 300 °C (CC300) and 650 °C (CC650), (b) palm kernel shell biochar (PK) charred at 300 °C (PK300) and 650 °C (PK650), (c) cocoa pod husk biochar (CP) charred at 300 °C (CP300) and 650 °C (CP650), rice husk biochar (RH) charred at 300 °C (RH300) and 650 °C (RH650).
Table 2
Kinetic parameters related to the adsorption of phosphate onto corn cob biochar (CC300 and CC650), palm kernel shell biochar (PK300 and PK650), cocoa pod husk biochar (CP300 and CP650) and rice husk biochar (RH300 and RH650).

| Kinetics models | Biochar | CC300 | CC650 | PK300 | PK650 | CP300 | CP650 | RH300 | RH650 |
|-----------------|---------|-------|-------|-------|-------|-------|-------|-------|-------|
| Experimental $Q_0$ (mg g$^{-1}$) | | 3.6 | 6.5 | 5.0 | 9.4 | 3.0 | 6.0 | 3.9 | 7.6 |
| Pseudo-first-order | | | | | | | | | |
| Calculated $q_e$ (mg g$^{-1}$) | | 2.8 | 4.5 | 3.5 | 10.9 | 2.6 | 5.4 | 2.6 | 4.7 |
| $K_1$ (h$^{-1}$) | 0.21 | 0.18 | 0.17 | 0.38 | 0.47 | 0.37 | 0.26 | 0.26 | 0.46 |
| $R^2$ | 0.94 | 0.76 | 0.94 | 0.90 | 0.85 | 0.79 | 0.87 | 0.85 | |
| Pseudo-second-order | | | | | | | | | |
| Calculated $q_e$ (mg g$^{-1}$) | | 4.2 | 7.7 | 5.2 | 10.3 | 2.9 | 6.2 | 4.2 | 8.2 |
| $K_2$ (mg g$^{-1}$ h$^{-1}$) | 0.11 | 0.05 | 0.12 | 0.06 | 0.22 | 0.09 | 0.15 | 0.08 | |
| $R^2$ | 0.99 | 0.90 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | |
| Elovich | | | | | | | | | |
| $\alpha$ (mg g$^{-1}$ h$^{-1}$) | 4.14 | 3.25 | 8.85 | 22.94 | 39.25 | 14.27 | 5.51 | 8.41 | |
| $\beta$ (mg g$^{-1}$) | 1.17 | 0.55 | 1.03 | 0.54 | 2.70 | 0.96 | 1.16 | 0.50 | |
| $R^2$ | 0.95 | 0.93 | 0.99 | 0.99 | 0.95 | 0.95 | 0.97 | 0.91 | |
| Intraparticle diffusion | | | | | | | | | |
| $K_i$ (mg g$^{-1}$ h$^{-1}$) | 0.28 | 0.63 | 0.33 | 0.36 | 0.11 | 0.38 | 0.30 | 0.58 | |
| $C$ (mg g$^{-1}$) | 2.00 | 3.90 | 2.50 | 5.30 | 1.91 | 3.05 | 1.68 | 3.00 | |
| $R^2$ | 0.72 | 0.65 | 0.81 | 0.82 | 0.65 | 0.85 | 0.84 | 0.66 | |

3.2. Effect of contact time on PO$_4$-P adsorption

Fig. 2 shows contact time effect of PO$_4$-P adsorption onto the biochars at the two pyrolysis temperatures, 300 °C and 650 °C. The results showed that the adsorption of PO$_4$-P from solution onto the biochars significantly ($p < 0.05$) increased in the first few hours and progressively remained stable until approaching an apparent equilibrium varying from 6 to 15 h. The initial rapid phase and the proceeding slow phase of PO$_4$-P adsorption is a commonly observed phenomenon (Saeed et al., 2005; Pellera et al., 2012). For a porous adsorbent such as biochar, the initial rapid adsorption phase likely reflected surface adsorption while the subsequent slow phase reflected diffusion of PO$_4$-P into the pores. The equilibrium time for maximum PO$_4$-P adsorption was faster for the 300 °C-biochars than the biochars types pyrolyzed at 650 °C. This can be explained by their higher CEC and lower Fe and Al contents (Table 1).

To predict and understand the PO$_4$-P kinetics adsorption mechanism, three popular chemical kinetics mathematical models were used, namely pseudo-first-order (PFO), pseudo-second-order (PSO) and Elovich models (Ho, 2006).

\[
\frac{d q_t}{d t} = K_1 (q_e - q_t) \quad \text{Pseudo-first-order}
\]

\[
\frac{d q_t}{d t} = K_2 (q_e - q_t)^2 \quad \text{Pseudo-second-order}
\]

\[
\frac{d q_t}{d t} = \alpha \exp(-\beta q_t) \quad \text{Elovich}
\]

Here $q_t$ (mg g$^{-1}$) and $q_e$ (mg g$^{-1}$) are the amount of P adsorbed at time $t$ and at equilibrium, respectively, $K_1$ (h$^{-1}$) and $K_2$ (mg g$^{-1}$ h$^{-1}$) are the PFO and PSO adsorption rate constants, respectively, $\alpha$ (mg g$^{-1}$ h$^{-1}$) is the initial adsorption rate and $\beta$ (g mg$^{-1}$) is the desorption constant.

PFO and PSO describe the kinetics of the solid-solution system based on physisorption and chemisorption, respectively, with regards to the adsorbent capacity (Ho, 2006). The Elovich model, which was formally used to elucidate the gas adsorption phenomenon, is now widely used to describe the aqueous contaminants sorption by assuming a strong heterogeneity of the sorbent surface (Plazinski et al., 2009). It is an empirical equation which accounts for the contribution of desorption (Yao et al., 2011).

PSO provided a better description of the kinetics of PO$_4$-P adsorption than PFO (Fig. 3, Table 2). Aside the high linear dependency of $q_t$ on $t$ ($R^2 = 0.99$), the calculated $q_e$ values of the PSO were closer to the experimental values ($Q_e$). Thus, the adsorption of PO$_4$-P onto the biochars was better characterized by the PSO and thereby occurred through chemisorption (Ho, 2006). The adsorption rate constant, $K_2$ (mg g$^{-1}$ h$^{-1}$) ranged from 0.05 to 0.22 mg g$^{-1}$ h$^{-1}$, relatively lower for biochar produced at 650 °C. The higher $K_2$ values for the 300 °C-biochars demonstrate an increase rate of PO$_4$-P adsorption on these adsorbents than the 650 °C-biochars with time.

The Elovich model also fitted the data well for all the biochar types ($R^2 > 0.90$) (Table 2). The adsorption rate, $\alpha$, varied among all the adsorbents (3.25 to 39.25 mg g$^{-1}$ h$^{-1}$). Desorption constant, $\beta$ increased in the order of RH650 < PK650 < CC650 < CP650 < PK300 < RH300 < CC300 < CP300. Obviously, the $\beta$ values were relatively higher for the 300 °C-biochars than the 650 °C-biochars implying a higher desorption of adsorbed PO$_4$-P. With regards to the assumption underlying the Elovich model, the active surface sites on the biochars used in the study are heterogeneous and therefore exhibit different activation energy for chemisorption.
For a porous adsorbent such as biochar, the diffusion mechanism of PO$_4$-P into it is of importance in the adsorption processes. Nonetheless, the chemical kinetics models cannot describe the diffusion mechanism. Intraparticle diffusion model was therefore deployed (Weber and Morris, 1963).

$$ q_t = K_i t^{1/2} + C \quad \text{Intraparticle diffusion} $$

Here, $K_i$ is the intraparticle diffusion rate constant (g µg$^{-1}$) and $C$ (g µg$^{-1}$) is a constant associated to the boundary layer thickness, both can be obtained from the plot of $q_t$ versus $t^{0.5}$ (Fig. 4).

PO$_4$-P adsorbed showed a high linear dependency on the square root of time ($R^2 > 0.60$), implying that intraparticle diffusion played a role in controlling PO$_4$-P adsorption on the biochar types. However, since the $C$ values are greater than zero ($C > 0$) (Table 2), intraparticle diffusion is not the sole rate limiting step. The earlier and later portions of the plot are the film diffusion and intraparticle adsorption stages, respectively. The $K_i$ values for the 650 °C-biochars was higher than the 300 °C-biochar types, which could be due to the highly porous nature of biochar produced at high temperatures (Zhang et al., 2015b). The lower values of $C$ observed for 300 °C- biochars implies that with reference to the rate-limiting step in the overall sorption process in these biochar types, surface film diffusion was less involved.

The validity of the intraparticle model coupled with Elovich and PSO in the present study suggests that PO$_4$-P adsorption was initially controlled by chemisorption and subsequently by intraparticle diffusion. These findings are in agreement with the results on P adsorption onto mallee biochar (Zhang et al., 2016).
3.3. Effect of pH on PO$_4$-P adsorption

The amount of PO$_4$-P adsorbed onto the biochars was highly related to pH (Fig. 5). This implies that pH played a major role in the entire adsorption process, particularly on the speciation of PO$_4$-P and the surface charge of the biochar and therefore its adsorption capacity. The amount of PO$_4$-P adsorbed was inversely related to the equilibrium pH (2.8 to 9.6) for the biochar types (Fig. 5). Biochar mostly has low point of zero charge (PZC) (Mukherjee et al., 2011) and therefore at pH > 4.5 negative surface charges will be created resulting in low PO$_4$-P sorption (Xie et al., 2014). The PAS-FTIR analysis indicated ample amounts of oxygen-containing functional groups among which is carboxylate (–COOH) that contributes considerably to the negative surface charge of the biochar types (Fig. 1). The surface negative potential of biochar decreases with increasing equilibrium pH (Li et al., 2017). Thus, the low affinity of PO$_4$-P by the biochars at high solution pH could be a result of the increased electrostatic anion repulsion between the negatively charged biochar surfaces and the negatively charged PO$_4$-P ions, and also because of increased competitive effect of OH$^-$. The equilibrium pH for maximum PO$_4$-P adsorption onto the biochar types was between 2.6 and 4.8. This was in line with equilibrium pH i.e. 3.0 to 6.5 reported for maximum PO$_4$-P sorption by potato, canola and walnut shell biochar (Feizi and Jalali, 2014). At the observed equilibrium pH (2.6 to 4.8) of the present study, Fe and Al would be active in solution. However, Ca and Mg would be precipitating or polymerizing out of solution. The presence of Fe and Al, may in part explain PO$_4$-P adsorption on the biochar types. This collaborated with the results of Shepherd et al. (2017), mapping the
3.4. Changes in pH and mechanism of PO$_4$-P adsorption

To fully comprehend the mechanisms of PO$_4$-P adsorption onto the biochar types, the ΔpH values (difference between equilibrium pH of biochar sample with PO$_4$-P solution and equilibrium pH of blank) were calculated (Table 3). In accordance with the ΔpH values, there was no change in pH with decreasing PO$_4$-P adsorption for PK650, RH300, RH650, CP300, CC300 and CC650 since the ΔpH were below 0.5 pH units (Nartey et al., 2000). However, CP650 and PK300 showed respective increase and decrease in pH which were more than pH 0.5 units. The 0.5 units increase in the ΔpH of CP650 coincided with the maximum PO$_4$-P sorption capacity (Table 3), indicating the release of hydroxyl ions (OH$^-$) during the adsorption process. Similarly, the maximum PO$_4$-P adsorption of PK300 coincided with a 0.7 unit decrease in pH (Table 3), implying the release of protons (H$^+$ or H$_2$O$^+$) during the adsorption process.

From the kinetics adsorption study, PO$_4$-P adsorption onto the biochars occurred predominantly through chemisorption (Table 2). The maximum PO$_4$-P sorption for CP300, RH650 and CC650 occurred at equilibrium pH from 3.2 to 3.4. Within this equilibrium pH range (3.2 to 3.4), Fe and Al from the ash in the biochar will exists as free Fe$^{3+}$ and Al$^{3+}$ ions (Marion et al., 1976). At this equilibrium pH range, 95% of PO$_4$-P exists as H$_2$PO$_4^-$ and only 5% as HPO$_4^{2-}$ since pK1 of PO$_4$-P is 2.15 (Lindsay, 1979). Surface precipitation of adsorbed PO$_4$-P with Fe and Al on CP300, RH650 and CC650 will thus occur (Eqs. (2) and (3)).

$$\text{Fe}^{3+} + 3\text{H}_2\text{PO}_4^- \rightarrow \text{Fe(H}_2\text{PO}_4)_3$$

(2)

$$\text{Al}^{3+} + 3\text{H}_2\text{PO}_4^- \rightarrow \text{Al(H}_2\text{PO}_4)_3$$

(3)

Phenol group (–OH) was identified on CP300, RH650 and CC650 and can remove PO$_4$-P through ligand exchange. Maximum adsorption for CP300, RH650 and CC650 were observed between equilibrium pH 3.2 and 3.4. These pHs are 5.6 to 5.8 pH units below the pKa of –OH (pKa = 9.0) (Evangelou, 1998). Thus, the –OH functional groups would be protonated. At these equilibrium pHs, the dominant PO$_4$-P species in solution is H$_2$PO$_4^-$. PO$_4$-P removal from the solution by the protonated phenol may occur via ligand exchange (Eq. (4)) and electrostatic attraction (Eq. (5)).

$$R - \text{OH}_2^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{RHO}_2\text{PO}_4 + \text{H}_2\text{O}$$

(4)

$$R - \text{OH}_2^- + \text{H}_2\text{PO}_4^- \rightarrow R - \text{OH}_2\text{H}_2\text{PO}_4$$

(5)

Because there were no changes in solution pH after adsorption, Eqs. (4) and (5) are also plausible. In Eq. (3), the PO$_4$-P is retained and could be exchanged by other anions (e.g. Cl$^-$, NO$_3^-$) back into solution. In Eq. (4), however, structural –OH is replaced and the PO$_4$-P is locked up. This mechanism may be ideal for water cleansing.

Carboxylic (–COOH), a functional group with pKa value of 4.8 (Sparks 1995) was found on RH300 and CC300. The equilibrium pHs for maximum PO$_4$-P adsorption were 2.6 and 2.7 for RH300 and CC300, respectively. The equilibrium pHs (2.6 and 2.7) were more than 2 pH units below the pKa of –COOH and therefore it will be protonated. The removal of PO$_4$-P by the protonated –COOH can occur via electrostatic attraction (Eq. (6)). Again, with no change in equilibrium pH as a result of adsorption, Eq. (6) is plausible. PO$_4$-P adsorbed by RH300 and CC300 is weakly held (electrostatic attraction) and can, therefore, easily be exchanged by other anions in the solution.

$$R - \text{COOH}_2^+ + \text{H}_2\text{PO}_4^- \rightarrow R - \text{COOH}_2\text{H}_2\text{PO}_4$$

(6)

The maximum PO$_4$-P adsorption capacity of PK650 occurred at equilibrium pH of 3.6. At this pH, and with the presence of Fe$^{3+}$ and Al$^{3+}$, there could be species of FeOH$_2^+$ and AlOH$_2^+$ in the solution (Marion et al., 1976). There was also no change in equilibrium pH after adsorption. Thus, in addition to surface precipitation (Eqs. (2) and (3)), PK650 can also adsorb PO$_4$-P by ligand exchange (Eqs. (7) and (8)).

$$\text{Fe} - \text{OH}_2^- + \text{H}_2\text{PO}_4^- \rightarrow \text{Fe} - \text{O} - \text{H}_2\text{PO}_3 + \text{H}_2\text{O}$$

(7)

$$\text{Al} - \text{OH}_2^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{Al} - \text{O} - \text{H}_2\text{PO}_3 + \text{H}_2\text{O}$$

(8)

The equilibrium pH (4.1) at which maximum PO$_4$-P adsorption occurred on PK300 coincided with a 0.7 unit decrease in equilibrium pH, implying a release of proton after PO$_4$-P adsorption. At the equilibrium pH of 4.1, Fe$^{3+}$, Al$^{3+}$, FeOH$_2^+$, AlOH$_2^+$, FeOH$^{2+}$ and AlOH$^{2+}$ all exist in solution monomeric forms of Fe and Al (Marion et al., 1976). At this equilibrium
|                  | Corn cob biochar         | Palm kernel shell biochar | Cocoa pod husk biochar | Rice husk biochar |
|------------------|--------------------------|---------------------------|------------------------|-------------------|
|                  | CC300                    | PK300                     | CP300                  | RH300             |
|                  | CC650                    | PK650                     | CP650                  | RH650             |
| ∆pH\(^a\)        | PO₄-P adsorbed (mg g\(^{-1}\)) | PO₄-P adsorbed (mg g\(^{-1}\)) | PO₄-P adsorbed (mg g\(^{-1}\)) | PO₄-P adsorbed (mg g\(^{-1}\)) |
| -0.2             | 3.64                     | 0.0                       | 5.99                   | 0.1               |
| 0.3              | 3.59                     | 0.2                       | 6.25                   | -0.7              |
| -0.2             | 3.25                     | -0.2                      | 5.79                   | -0.1              |
| -0.3             | 2.90                     | -0.3                      | 5.46                   | -0.2              |
| -0.1             | 2.55                     | -0.1                      | 4.45                   | -0.2              |
| 0.1              | 1.92                     | -0.3                      | 3.50                   | -0.2              |
| 0.3              | 1.75                     | 0.4                       | 2.85                   | 0.0               |

\(^a\) The difference between equilibrium pH of biochar sample with PO₄-P solution and equilibrium pH of blank without PO₄-P solution.
pH (4.1), 95% of PO₄-P exist as H₂PO₄⁻ and 5% as H₃PO₄ (Lindsay, 1979). PO₄-P adsorption by PK300 can, therefore, occur by precipitation and ligand exchange with a concomitant release of protons (Eqs. (9)–(14)).

\[
\begin{align*}
\text{Fe}^{3+} + 2\text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_2\text{H}_2\text{PO}_4 + 2\text{H}^+ & (9) \\
\text{Al}^{3+} + \text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_2\text{H}_2\text{PO}_4 + 2\text{H}^+ & (10) \\
\text{Fe} - \text{OH}^{2+} + \text{H}_2\text{PO}_4^- & \rightarrow \text{FeH}_2\text{PO}_4 + \text{H}^+ & (11) \\
\text{Al} - \text{OH}^{2+} + \text{H}_2\text{PO}_4^- & \rightarrow \text{Al} - \text{O} - \text{H}_2\text{PO}_3 + \text{H}^+ & (12) \\
\text{Fe} - \text{OH}^+ + \text{H}_2\text{PO}_4^- & \rightarrow \text{Fe} - \text{O} - \text{H}_2\text{PO}_3 + \text{H}_2\text{O}^+ & (13) \\
\text{Al} - \text{OH}^+_2 + \text{H}_2\text{PO}_4^- & \rightarrow \text{Al} - \text{O} - \text{H}_2\text{PO}_3 + \text{H}_3\text{O}^+ & (14)
\end{align*}
\]

However, as the decrease in pH was only 0.7 pH units, it is unlikely that Eqs. (9) and (10) occurred since these equations depict the release of 2 moles of H⁺ that would have accounted for a greater decrease in pH. The more plausible reactions are thus Eqs. (11)–(14).

The maximum PO₄-P adsorption onto CP650 occurred at an equilibrium pH of 3.2. At this pH the –COOH will exist mainly in its neutral form. PO₄-P adsorption by –COOH can occur via ligand exchange with a concomitant release of OH⁻ ions (Eq. (15)).

\[
\text{RCOOH} + \text{H}_2\text{PO}_4^- \rightarrow \text{RCOOH}_2\text{PO}_4 + \text{OH}^-
\]

In summary, the mechanisms of PO₄-P adsorption onto the biochar types were diversiform, mainly including electrostatic attraction, surface precipitation and ligand exchange; which depended largely on the feedstock and the pyrolysis temperature.

4. Conclusion

The study indicated that the biochar types have affinity for PO₄-P adsorption. PO₄-P adsorption was faster on the low pyrolysis biochar types (300 °C) as compared to their counterparts (650 °C). Increasing pyrolysis temperature proportionally increased the PO₄-P adsorption. Maximum PO₄-P adsorption on the biochar types occurred at low pHs (2.6–4.8). The adsorption of PO₄-P onto the heterogeneous surface of the biochar types was predominantly controlled by intraparticle diffusion and chemisorption (electrostatic attraction, surface precipitation and ligand exchange). The use of RH300 and CC300 present an interesting option for waste recycling as a slow PO₄-P releasing fertilizer. PK, CP, CC650 and RH650 can also serve as a strong PO₄-P adsorbent in tertiary wastewater treatment since the PO₄-P adsorbed (surface precipitation and ligand exchange) cannot easily be desorbed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Joseph Osafo Eduah: Conceptualization, Methodology, Investigation, Visualization, Formal analysis, Writing - original draft. Eric Kwesi Nartey: Supervision, Methodology, Writing - review & editing. Mark Kofi Abekoe: Supervision, Methodology, Writing - review & editing. Stephan Weck Henriksen: Investigation, Resources, Formal analysis. Mathias Neumann Andersen: Writing - review & editing, Funding acquisition.

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