Recovery of phosphate with chemically modified biochars

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Highlights

- Biochar phosphate uptake can be enhanced from relatively low levels (e.g. 2.1% - 3.6%) to relatively high levels (66.4% - 70.3%) by impregnation with magnesium.
- Biomass pre-treatment with magnesium salts were markedly higher than those of biochar post-treatment.
- Biochar post-treatment with alkali also improved phosphate uptake capacity but was not a function of biochar surface area.

Abstract

The use of biochar for the recovery of phosphate has potential for environmental and socio-economic benefits but it is often characterised by relatively low nutrient adsorption capacity. The aim of this study was to investigate the potential for improving biochar phosphate adsorption capacities following chemical modification with metal salts, acids and alkali. Modified biochars were produced from oak wood and paprika waste (greenhouse waste) following either chemical treatment of biomass (in-situ modification) or biochar (post modification). Other chemical
treatments investigated included chemical oxidation, activation and salt treatment. Phosphate uptake capacities were determined by laboratory batch sorption tests, and results indicated that phosphate adsorption could be enhanced from relatively low levels (2.1% - 3.6%) to relatively high levels (66.4% - 70.3%) by impregnation with magnesium. These findings suggest that biochar mineral composition is a key property influencing biochar phosphate uptake capacity while surface area has less influence on sorption.

Key words: Biochar modification; Biomass pre-treatment; Phosphate sorption.

1. Introduction

Phosphates are essential plant nutrients but growing concerns about its future availability as well as its effects in water bodies (eutrophication) have made its recovery important (Rittmann et al. 2011; Wang et al. 2015a; Zeng et al. 2013). Recovery of phosphate is also necessary as it can be present at high concentrations in various agricultural and industrial wastewaters (Cai et al. 2013). Some studies have shown that biochars, the solid products formed from the thermochemical treatment of various kinds of organic matter, are capable of adsorbing various species including phosphates (PO$_4$-P) (Laird et al. 2010; Wang et al. 2015a; Yao 2013; Zeng et al., 2013; Zheng et al. 2010). Some studies have also reported that biochars are capable of releasing adsorbed PO$_4$-P, implying that such biochars could complement fertilizer use (Zheng et al. 2010). Nguyen et al. (2014) however observed that most agricultural by-products considered for environmental management including phosphate recovery require some form of modification. Indeed, there is growing interest in modifying biochar properties to enhance their adsorption capacities and other properties such
that “bespoke” or even smaller quantities of biochars are required for soil amendment 
(Eberhardt et al. 2006; Novak et al. 2009; Silber et al. 2010; Wang et al. 2015a).

Ongoing research considers the development of waste-derived biochars with superior 
sorption capacities and involves various treatment processes which can be broadly 
categorised as liquid phase (chemical activation), gas phase (physical activation with 
steam or carbon dioxide) or surface modification with chemicals, the lattermost not 
always requiring a carbonisation step (Krishnan and Haridas 2008). Physical and 
chemical activation treatments are more frequently employed, possibly because such 
treatments offer greater improvements in char surface area and porosity development 
due to the higher activation temperatures employed (T>450°C). Despite the lower 
temperatures used in surface modification (60-80°C) however, comparable 
improvements to surface area have been observed by Sricharoenchaikul et al. (2008).

Compared to physical activation, it has been suggested that chemical activation can 
be cheaper, less time-consuming, and may provide more opportunities for char 
porosity development (Krishnan and Haridas 2008; Lillo-Ródenas et al. 2003; Marsh 
and Rodríguez-Reinoso 2006; Sricharoenchaikul et al. 2008). Moreover, in physical 
activation, porosity development is achieved at the expense of carbon yield in some 
cases (Viswanathan et al. 2009). Conversely, chemical agents within the carbon 
feedstock might improve microporosity by interfering with the reduction in volume 
which is known to occur as processing temperature increases, and by leaving behind 
new pores when such agents are washed off (Marsh and Rodríguez-Reinoso 2006).

Consequently, chemical activation agents are frequently used, and include transition 
metal salts, potassium and sodium hydroxides (Chen et al. 2011; Marsh and 
Rodríguez-Reinoso 2006; Park et al. 2015). Other studies have focused on increasing 
acidic surface functional groups via oxidation or acid treatment (Kastner et al. 2009;
Moreno-Castilla et al. 2000; Sricharoenchaikul et al. 2008; Xue et al. 2012), since studies have shown that acidic and basic surface oxides are responsible for black carbon cation and anion exchange properties respectively (Boehm 1994).

In terms of improving biochar properties for $\text{PO}_4$-$\text{P}$ removal, studies have demonstrated that the presence of basic oxygen functional groups such as metal oxides, ketones, pyrones and chromens can improve biochar $\text{PO}_4$-$\text{P}$ uptake (Chen et al. 2011; Nyugen et al. 2012, 2014; Park et al. 2015; Wang et al. 2015a; Xue et al. 2009; Yao 2013; Zeng et al. 2013). Various processing temperatures, activating agents and loading ratios have been employed, which understandably produce adsorbents with different $\text{PO}_4$-$\text{P}$ sorption capacities even when similar chemical activation agents are used. For instance, while some studies have reported improvements in adsorbent $\text{PO}_4$-$\text{P}$ uptake following Fe-treatment (Krishnan and Haridas 2008; Nyugen et al. 2013), about 51% decrease has been observed in other studies (Yao 2013). This study was therefore aimed at contributing to growing research on the optimal parameters required for obtaining biochars with superior $\text{PO}_4$-$\text{P}$ uptake hence improving their agronomical value. Consequently, the $\text{PO}_4$-$\text{P}$ sorption capacities of biochar derived from traditionally used biomass (oak) and agricultural waste (paprika waste) with comparable carbon contents (>40%) were evaluated following activation with various chemical agents to understand the effect of these treatments on biochar $\text{PO}_4$-$\text{P}$ recovery. Furthermore, the effect of treatment route (i.e. biomass pre-treatment versus biochar post-treatment) was investigated for chemical treatments which demonstrated the greatest improvements in biochar $\text{PO}_4$-$\text{P}$ uptake.

2. Methods

2.1 Facilities
Biochars produced from holm oak were obtained from a commercial pyrolysis plant operated by Proininso (Spain) at 450 °C and 650 °C (designated OAK 450 and OAK 650 respectively). Biochar produced from greenhouse paprika waste possessing comparable carbon content to OAK 450 and OAK 650 was produced by the Energy research Centre of the Netherlands (ECN) at 400 °C, and designated GHW 400.

2.2 Biochar and biomass treatment

All chemicals used for biochar and biomass treatment were of analytical grade and used as-received.

2.2.1 Chemical activation with metal chloride salts

Following a methodology similar to that of Zhang et al. (2012), 10 g oak biochars were mixed with 40 g FeCl₃·6H₂O in 60 mL distilled water iron chloride hexahydrate, stirred thoroughly and left to stand for 2 h at room temperature. The mixture was heated for 24 h at 100 °C on a Stuart hotplate before pyrolyzing biochar for 1 h in a nitrogen atmosphere at 5 mL min⁻¹ and heating rate of 10 °C min⁻¹ at 400 or 600 °C depending on the biochars’ original production temperatures. That is, OAK 450 was pyrolyzed at 400 °C while OAK 650 was pyrolyzed at 600 °C to correspond with temperatures slightly below initial production temperatures. Modified biochars were subsequently rinsed with distilled water and oven dried at 100 °C for 2 h. This procedure was repeated for biochars treated with MgCl₂·6H₂O on oak biochars with particle size ≤ 850 µm, ≤ 2 mm and ≤ 4.75 mm.

Additional magnesium treatments were performed: to compare the effect of magnesium treatment route (in situ treatment versus biochar post-treatment), as-received holm oak chips and greenhouse waste biomass were treated with
MgCl$_2$·6H$_2$O as outlined above and pyrolyzed at 600 °C. Secondly, to investigate the effect of pyrolysis temperature on magnesium loading onto already-made biochars, OAK 650 was pyrolyzed at 400 and 600 °C and stored for PO$_4$-P sorption analysis.

2.2.2 Surface and chemical activation with KOH

For surface activation, 4 g of biochar (particle size ≤ 2 mm) was mixed in a solution of 2 g KOH and 20 mL of distilled water. The mixture was stirred for 2 h at 75 °C with a magnetic stirrer. The treated biochars were subsequently rinsed with HCl followed by distilled water until the leachate pH values ranged between 6-7 then oven-dried for 2 hours at 100 °C. This treatment was done for OAK 450, OAK 650 and GHW 400 biochars.

For chemical activation of oak biochars, the same procedure as outlined for surface modification was performed but with an additional pyrolysis step, where OAK 450 and OAK 650 were pyrolyzed for 1 h in a nitrogen atmosphere at 5 mL min$^{-1}$ and heating rate of 10 °C min$^{-1}$ at 400°C and 600 °C respectively. Treated biochars were washed and dried as outlined above.

To compare the effect of KOH activation on raw biomass, 4 g holm oak and greenhouse waste were each soaked in 20 mL distilled water containing 2 g KOH followed by pyrolysis in nitrogen at 5 mL min$^{-1}$ at 600 °C for 1 h at a heating rate of about 10 °C min$^{-1}$. Biochars were rinsed with HCl followed by distilled water until the leachate pH values ranged between 6-7 and oven–dried for 2 h at 100 °C.

2.2.3 Surface activation with H$_2$O$_2$

2 g biochars of particle size ≤ 2 mm were soaked in 20 mL of 10% and 30% H$_2$O$_2$ for 48 h at room temperature, using a methodology similar to that of Moreno-Castilla et
al. (2000) and Xue et al. (2012) without agitation, after which biochars were heated at 80 °C for 24 h, washed with distilled water until the pH was between 6-7 and oven dried.

2.3 Agronomical analyses

Ultimate analyses of biochar samples were determined using a CHN Elemental Analyser (Thermo Scientific Flash 2000). Proximate analysis was performed in a muffle furnace. Macro- and micro-nutrient content of the chars was determined after acid digestion of chars in concentrated nitric acid and analyzed by Inductively-coupled Plasma-Mass Spectroscopy (ICP/MS, Perkin Elmer ELAN DRC ICP-MS) (Perkin Elmer). pH measurements with a pH meter (Hach Lange) were made after 1:20 char/distilled water mixtures were shaken and allowed to stand for 2 h. Scanning Electron Microscopy (SEM) and Electron Dispersive X-ray Spectroscopy (EDS) was performed on biochars using a Carl Zeiss EVO MA15 SEM with Oxford Instruments AZtecEnergy EDX system. Brunauer-Emmett-Teller (BET) surface area and pore size distribution of treated and untreated biochars were determined by N$_2$ gas adsorption (Tristar 3000 Micromeritics) at -196 °C after outgassing at 120 °C for 2 h. BET surface area was determined from linear fit adsorption data generated while pore volumes were determined using the t-plot model. Total pore volumes were obtained at relative N$_2$ pressures of 0.99. Spectral analysis was performed using an iS10 Nicolet Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectrophotometer, taking 64 scans over a range of 4000-400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$.
Cation exchange capacity (CEC) was determined using a method similar to that of Brewer (2012) and Yuan et al. (2011). 20 mL distilled water was added to 1 g of biochar and shaken at 160 rpm for 10 min each in a water shaker bath (SW23 Julabo GmbH) at room temperature and filtered through a Whatman Grade 1 filter paper. This was repeated four more times, discarding the leachates each time. Biochars were saturated with 10 mL of 1 M sodium acetate with pH adjusted to 7 using a few drops of glacial acetic acid, shaken at 160 rpm for 16 min and filtered. This was repeated twice more, discarding the leachates each time, after which biochars were rinsed with ethanol thrice for 8 min each at 160 rpm. Three additions of 1 M ammonium acetate at pH 7 were used to displace sodium cations by shaking at 160 rpm for 16 min, storing the leachates for subsequent analysis. Analyses were done in duplicate and the average values are reported. The concentration of displaced sodium cations were determined by Atomic Absorption Spectroscopy (AAS) of 10 mL aliquots of the final leachates following the addition of 10 mL 2000 ppm KCl as ionization-suppressant.

2.4 Phosphate sorption tests

As anaerobic digestion plants and other agricultural and industrial wastewaters are known to possess considerably high PO$_4$-P concentrations, about 125 mg P L$^{-1}$ was used in this study to investigate biochar PO$_4$-P removal efficiency. A small number of biochars were also tested at 21.3 mg P L$^{-1}$ for comparative purposes, as previous studies have often evaluated adsorbent performance at this concentration range.

2.4.1 Batch adsorption

All containers were acid washed in a 1 M HCl bath and rinsed with deionised water before use. 0.1 g biochar (≤850 µm) was transferred to plastic Nalgene containers and 100 mL of phosphate solution prepared from potassium phosphate monobasic.
was added after its pH was adjusted to 7 with NaOH. The containers were sealed tightly and the mixtures shaken at 160 rpm for 24 h in a water shaker bath (SW23 Julabo GmbH) at room temperature, after which 10 mL aliquots of each sample were filtered through 0.45 µm Sartorius Minisart syringe filters for Ion Chromatography analysis (Metrohm 850 Professional IC). Most analyses were done in duplicate and the average values reported. The concentrations of adsorbed ions were determined as:

$$q_e = \frac{(C_o - C_e)}{M}$$  \hspace{1cm} (1)

Removal efficiency was determined as:

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100$$  \hspace{1cm} (2)

where $C_o$ and $C_e$ = initial and equilibrium liquid-phase phosphate adsorbate concentrations respectively (mg L$^{-1}$); $V$ = volume of solution (L); $M$ = mass of biochar sample used (g).

2.4.2 Desorption isotherms

Biochars which had previously undergone phosphate adsorption as outlined in Section 2.4.1 were filtered through a Whatman Grade 1 filter paper and desorption was done by extracting phosphate from biochars using 0.01 M KCl solution. The mixture was shaken at 160 rpm for 24 h in a water shaker bath at room temperature. Analysis was carried out in duplicate, and 10 mL aliquots of each sample were taken
after 24 h then filtered through 0.45 µm Sartorius Minisart syringe filters for Ion Chromatography analysis.

2.4.3 Adsorption kinetics

To investigate possible phosphate adsorption mechanisms in biochars, a selection of biochars (≤850 µm) were added to about 400 mg PO₄ L⁻¹ solutions as done in Section 2.4.1 but 10 mL aliquots of each sample were taken at 2.5, 5, 7.5, 10 and 24 h then filtered through 0.45 µm Sartorius Minisart syringe filters for Ion Chromatography analysis. Adsorbate concentrations withdrawn at intervals were determined using Equation (3):

$$q_t = \left( C_o - C_t \right) \frac{V}{M} \quad (3)$$

where $q_t$ = amount of PO₄²⁻ adsorbed (mg g⁻¹); $C_o$ and $C_t$ = liquid-phase adsorbate concentrations at initial conditions and at time t respectively (mg L⁻¹).

3. Results and discussion

3.1 As-received biochar physicochemical properties

Table 1 presents key biochar physicochemical properties prior to chemical treatment. Biochar carbon contents were >50% as mandated by the IBI (IBI, 2014) and both oak and GHW biochars were alkaline. Oak biochar ash contents were lower than greenhouse waste biochar (GHW 400) and consequently possessed less macro-
minerals compared to GHW 400. GHW 400 also had the highest CEC (Fig. 1), followed by OAK 650. The higher CEC of OAK 650 relative to OAK 450 is contrary to the trend observed in biochars, wherein lower temperature chars possess more oxygen functional groups (Wang et al. 2015b) hence higher CEC.

FTIR spectra are presented in Fig. 2 for the 1800-600 cm\(^{-1}\) region as most band differences were observed in this region. The characteristic O-H stretching band around 3500-3200 cm\(^{-1}\) was absent in all biochars. Furthermore, the absence of bands at 3200 cm\(^{-1}\) suggested that the biochars did not possess furans (Keiluweit et al. 2010). In the 1800-600 cm\(^{-1}\) region, 4 bands were observed in all biochars: sharp peaks around 1714-1698 cm\(^{-1}\) attributable to C=O stretching of carbonyl groups (Pradhan and Sandle 1999; Wu et al. 2011); 1440 cm\(^{-1}\) likely corresponding to ketone stretching as observed in lignocellulosic materials (Keiluweit et al. 2010); 1400 cm\(^{-1}\) likely due to aromatic C=C stretching (Park et al. 2015); 875 cm\(^{-1}\) possibly due to out-of-plane bending vibrations for \(\beta\)-glucosidic linkages or for C-O groups, aldehydes and benzene derivatives (Krishnan and Haridas 2008; Sricharoenchaikul et al. 2008). Additional bands were also present in OAK 450 and GHW 400 biochars at 1610 cm\(^{-1}\), attributable to aromatic C=C stretching or conjugated ketone and quinone C=O stretching vibrations (Keiluweit et al. 2010; Park et al. 2015). A band at 1583-1575 cm\(^{-1}\) resulting from conjugated C=O stretching vibrations of hemicellulose or aromatic rings (Krishnan and Haridas 2008; Sricharoenchaikul et al. 2008).

In terms of PO\(_4\)-P removal efficiency, the highest PO\(_4\)-P uptake was observed in OAK 650 followed by GHW 400 (Fig. 3). Maximum PO\(_4\)-P uptake was achieved before 24 h: after 5 h in oak biochars and even earlier in GHW 400, possibly because of the high initial PO\(_4\)-P concentrations used in this study. No PO\(_4\)-P was detected from both
biochar types following desorption tests, suggesting that PO$_4$-P was strongly bound to
the char or that the extracting solution was inadequate.

3.2 Treated biochar physicochemical properties

As two types of chemical treatment were used to modify biochars, activating agents
are prefixed with “SA” and “CA” to represent surface activation and chemical activation
respectively, the latter treatment involving an additional pyrolysis step. Various
chemical treatments understandably had variable effects on biochar functionality as
outlined henceforth.

3.2.1 CEC and functional groups

Surface activation with KOH increased biochar CEC, with the highest improvement
observed in SA-KOH GHW 400 (Fig. 1). Min et al. (2004) have also observed CEC
improvements following surface modification with bases. CEC decreased following
treatments involving further pyrolysis steps (CA-KOH) however. For instance, while
SA-KOH treatment increased OAK 450 and OAK 650 CEC by about 82 and 56 cmol·
kg$^{-1}$ respectively, the reverse was observed in oak biochars after CA-KOH treatment.

It is uncertain whether the increase in GHW 400 CEC following SA-KOH treatment
can be attributed to oxidation of the biochar surface resulting from the presence of K
and O following Equation (4) as outlined in Viswanathan et al. (2009), because while
potassium salt complexes are formed even without carbonization (Ehrburger et al.
1986; Lillo-Ródenas et al. 2003), Equation (4) might only occur at much higher
temperatures (Ehrburger et al. 1986; Lillo-Ródenas et al., 2003; Viswanathan et al.
2009):

$$K_2O + C \rightarrow C-O-K + K$$ (4)
It is more likely that CEC improvements may have resulted from an increase in carbonyl groups. This hypothesis is based on the marked CEC increase observed in SA-KOH treatment of GHW 400 compared to oak biochars, the former biochar possessing more carbonyl groups as seen in Fig. 2(c) (1760-1665 cm\(^{-1}\) bands). Mallampati and Valiyaveettil (2013) reported ester bond cleavage into hydroxyl groups following NaOH treatment. Yakout (2015) also found that KOH treatment increased biochar phenolic groups; such base treatment is said to increase char CEC (Han et al. 2005). SA-H\(_2\)O\(_2\) treatment also improved CEC although not as greatly as surface treatment with SA-KOH treatment. This increase was possibly due to the formation of oxygen-containing species following acid-catalysed hydrolysis reactions (Lin et al. 2012; Marsh and Rodríguez-Reinoso 2006). FTIR spectra confirmed that some band intensities increased following some surface activation treatments, notably the 1700 cm\(^{-1}\) and 1440 cm\(^{-1}\) bands in GHW 400 after SA-KOH treatment (Fig. 2(c)). SA-KOH OAK 450 also possessed a marginally higher peak at 1585 cm\(^{-1}\) relative to untreated OAK 450. These suggest an increase in C=O groups. Following H\(_2\)O\(_2\) and Mg treatment, absorbance intensities either had no marked effect on biochar functional groups or decreased their intensities.

### 3.2.2 Surface area

SA-KOH treatment increased the surface area of GHW 400 by 55% while a drastic decrease of >75% was observed in SA-KOH treated oak biochars. An increase in GHW 400 surface area may have resulted from demineralization by KOH or HCl (the latter introduced during the rinsing stage of the procedure), as is known to occur following alkali or acid treatment of feedstocks (Mahmoud et al. 2012; Mukherjee 2003;
Yakout 2015). Demineralization from KOH action is more likely, since preliminary tests showed that increasing KOH/biochar loading ratios whilst maintaining the same HCl concentration improved surface areas in all 3 biochars. For instance, SA-KOH treated OAK 650 at 1:1 and 5:1 loading ratios had a surface area of 59.3 m² g⁻¹ and 67.8 m² g⁻¹ respectively. The demineralization was possibly more pronounced in GHW 400 owing to its higher ash content, especially if such inorganics were more loosely bound to its carbon structure than in oak biochars. Dislodgement of these inorganics would consequently increase pore spaces, although more studies are required to confirm this.

The decrease in oak biochar surface areas following SA-KOH treatment likely occurred because surface activation was not followed by high temperature treatment. This was validated by the fact that an additional pyrolysis step performed on OAK 650 increased its surface area to 344.3 m² g⁻¹. Yet a similar KOH surface activation process on physic nut waste biochar without further heat treatment resulted in an increase in surface area from about 200 m² g⁻¹ to >500 m² g⁻¹ in Srircharoenchaikul et al. (2008). As this study was aimed at improving biochar PO₄-P removal efficiency however, less emphasis was placed on increasing biochar surface area as it was observed that high and low surface area biochars performed comparably. This was further demonstrated by CA-KOH OAK 650 (i.e., OAK 650 pyrolyzed after KOH treatment) whose higher surface area did not improve its PO₄-P removal efficiency (as shown in Section 3.3.3).

Generally however, KOH treatment is known to significantly improve surface areas in feedstock (Azargohar and Dalai 2008; Gu and Wang 2012; Srircharoenchaikul et al. 2008) owing to intercalation of K atoms within carbon lamella. This results in an increase in char porosity following their removal in a rinsing step (Srircharoenchaikul
et al. 2008; Viswanathan et al. 2009) but such reactions may typically occur at high temperatures through the series of reactions outlined in Viswanathan et al. (2009).

Indeed in terms of porosity development, while chars benefit from H$_3$PO$_4$ and ZnCl$_2$ treatment at temperatures of <450 °C and <500 °C respectively, KOH treatment requires higher activation temperatures (Marsh and Rodríguez-Reinoso 2006).

Following a similar trend to SA-KOH treatment, a 46% increase was observed in GHW 400 after SA-H$_2$O$_2$ treatment while oak biochar surface areas decreased (53.3% and 73.1% for OAK 450 and OAK 650 respectively) with even greater reduction following 30% H$_2$O$_2$ treatment. Pereira et al. (2003) and Pradhan and Sandle (1999) respectively reported a 12% and 9.2% reduction in surface area following surface activation of activated carbon with <10% and 30% H$_2$O$_2$. It is not unusual for char surface areas to decrease following chemical treatment due to pore wall collapse (Moreno-Castilla et al. 2000; Pereira et al. 2003; Pradhan and Sandle 1999) or blockage of micropores by newly formed surface oxygen groups (Pradhan and Sandle 1999). However, Xue et al. (2012) and Yakout (2015) respectively reported that peanut hull hydrochar and rice straw biochar treated with 10% and 30% H$_2$O$_2$ increased char surface area by 7.7% and 55.4%. It remains unclear why H$_2$O$_2$ surface treatment has such variable effects, and further investigations are required to confirm whether compositional differences in ash content are influential factors.

### 3.2.3 Carbon content

While a decrease in carbon content between 13-23% was observed in OAK 650, carbon contents of OAK 450 and GHW 450 increased following most SA and CA treatments as seen in Table 2 due to a reduction in other elements. The increase in carbon content in OAK 450 and GHW 400 following SA-H$_2$O$_2$ was contrary to findings
of Xue et al. (2012). However, increases in hydrogen and oxygen content for all acid
treated biochars were observed, and this suggests the presence of stable carbon-
-oxygen complexes and available activated sites (Guerrero et al. 2005). These findings
suggest that benefits can be derived from chemical treatment in terms of improved
CEC and in some cases surface area without a great deal of material loss.
3.3 Influence of chemical treatment on biochar $\text{PO}_4^-$P uptake

3.3.1 Chemical activation with magnesium

Mg treatment of oak biochar resulted in much greater $\text{PO}_4^-$P uptake, particularly smaller particle size ($\leq 850 \mu$m) biochars. Fig. 3(b) shows that biochars treated with magnesium salts adsorbed the highest $\text{PO}_4^-$P, with Mg-OAK 650 adsorbing more $\text{PO}_4^-$P than Mg-OAK 450. To identify whether this was due to differences in biochar properties or to temperature, the $\text{PO}_4^-$P removal efficiencies of OAK 650 pyrolyzed at 400°C and 600°C were compared. $\text{PO}_4^-$P sorption was found to be much lower in the former suggesting that temperatures $>400$ °C are required for developing adequate $\text{PO}_4^-$P adsorbents. SEM/EDS of OAK 650 following Mg treatment at 600 °C confirmed the presence of Mg (Fig. 4(a)) while no visible differences were observed in OAK 450 °C after 400 °C Mg treatment (data not included). Some Mg$^{2+}$ was leached into the $\text{PO}_4^-$P solution during the test, as evidenced by the slightly lower count number seen in Fig. 4(b) and from ion chromatography data (data not included).

As there was a marked improvement to $\text{PO}_4^-$P uptake observed for 600 °C Mg treatment, this temperature was used for Mg-treatment of unpyrolyzed oak and greenhouse waste. Both Mg-treated biomass samples showed even greater $\text{PO}_4^-$P uptake compared to their Mg-treated biochar counterparts (Fig. 3) and compare favourably with adsorbents from previous studies (Table 3). Thus in-situ magnesium modification is more attractive than biochar post-treatment in terms of $\text{PO}_4^-$P uptake and cost, as a single-step modification and pyrolysis process is involved which reduces energy requirements. Following desorption tests, 8.9 mg g$^{-1}$ $\text{PO}_4^-$P was released from Mg-treated oak biomass, but was undetected in the case of greenhouse
waste biomass. Further investigations are required to better understand why PO₄-P release was low, as this impacts its potential for use as a soil fertilizer, or for repeated use in wastewater.

For both in-situ and post-treatment magnesium modification processes, coexisting ions were not found to have an adverse effect on PO₄-P uptake: from a 450 mg L⁻¹ solution of NH₄⁺ and PO₄³⁻, oak chips pyrolysed following Mg treatment (in-situ modification) recovered 66% and 72% PO₄-P at pH 7 and 8.5 respectively. This is expected, given that pH ranges >7 are typically used for struvite precipitation. Similarly, high PO₄-P removal efficiencies were maintained by in-situ modified greenhouse waste and oak chips in synthetic wastewater (Table 3). Other studies (Yao 2013; Zhang et al. 2009) similarly found that PO₄-P uptake was not greatly affected by coexisting ions.

3.3.2 Iron treatment

Ferric chloride treatment performed on oak biochars resulted in only modest improvements to PO₄-P removal efficiency. Yao (2013) found that surface modification of biochars with iron nitrate decreased PO₄-P uptake from pure PO₄-P solutions (pH 7) by about 51%. Conversely, Krishnan and Haridas (2008) and Nyugen et al. (2013) found that adsorbent treatment with iron nitrate and chloride salts improved PO₄-P uptake from pure PO₄-P solutions (pH 3).

Three hypotheses may be drawn from these studies: Fe-treated adsorbents may perform best in PO₄-P solutions with low pH; in other words, PO₄-P solution pH may be more important than the nature of Fe salt used for adsorbent modification. This is understandable given that anion exchange capacity is pH-dependent (Biswas et al. 2007; Zhang et al. 2009). While Wang et al. (2011) demonstrated that adsorbent
treatment with Fe$^{2+}$ salt improved PO$_4$-P adsorption capacity to a greater extent than
with Fe$^{3+}$ salt, maximum PO$_4$-P uptake was achieved at the lowest pH conditions for
both Fe$^{2+}$ and Fe$^{3+}$ treated adsorbents. Secondly, Fe treatment method may influence
adsorbent PO$_4$-P uptake. Nyugen et al. (2014) recommended the base treatment
(saponification) or oxidation of adsorbent materials prior to metal loading as evidence
suggests that such cationization processes improve the effectiveness of metal
deposition onto adsorbents, thus enhancing their PO$_4$-P removal efficiency. In one
study however (Carvalho et al. 2011), although adsorbent etherification prior to Fe$^{2+}$-
treatment improved adsorbent PO$_4$-P uptake, a comparable result was obtained by
non-etherified Fe$^{2+}$-treated adsorbent, with 97% and 93% removal efficiencies
respectively. Finally, it is reasonable for biomass or biochar composition to influence
the effectiveness of Fe treatment. From the few studies highlighted earlier however,
differences between high efficiency Fe-treated PO$_4$-P adsorbents (coir pith, sugarcane
bagasse, orange waste, activated carbon) and low efficiency Fe-treated adsorbents
(anaerobically digested sugar beet tailing biochar, oak biochar) are not readily
discernible. Yao (2013) however suggested that ferric hydroxide precipitates might
have coated biochar MgO (periclase), the latter likely being responsible for PO$_4$-P
uptake.

Overall, these findings suggest that surface activation of biochars with or without a
pre-treatment step is sufficient for improving adsorbent PO$_4$-P removal efficiency. pH
seems to influence Fe-loaded adsorbent PO$_4$-P removal efficiency to a larger extent
than adsorbent composition or treatment route. In other words, an additional pyrolysis
step following biochar treatment in Fe solutions may not be necessary.
3.3.3 KOH Treatment

SA-KOH treatment improved PO₄-P uptake by GHW 400, and previous studies (Samadi 2006; Sarkhot et al. 2013) have suggested ligand exchange between OH⁻ and PO₄³⁻. Further studies are required however, as FTIR did not show much hydroxyl groups present in GHW 400 and most other chars in this study. Furthermore, preliminary PO₄-P sorption tests on SA-KOH treated oak biochars showed some improvement in their PO₄-P removal efficiencies, but were comparable to CA-KOH treated oak biochars. Low PO₄-P uptake following similar CA-KOH treatment was also observed elsewhere (Park et al. 2015).

3.3.4 H₂O₂ Treatment

Figs. 3(a)-(c) show that H₂O₂-treated OAK 450 and GHW 400 did not improve PO₄-P uptake. The decrease in PO₄-P uptake by such treated GHW 400 may be due to a reduction in magnesium and other inorganic elements as earlier suggested, but further analysis is required to confirm this. This lack of improvement following acid treatment has also been observed elsewhere (Park et al. 2015), and may be attributed to the formation of greater negative functional groups on biochar surfaces after acid treatment (Wang et al. 2015b), which may have been the cause of decreased biochar adsorption capacity for anionic species.

3.4 PO₄-P adsorption kinetics

PO₄-P adsorption kinetics of unmodified biochars and some surface and chemically treated biochars were determined using the frequently used pseudo-first order, pseudo-second order and intraparticle diffusion models (Equations 5-7) with parameters determined from models’ plots:
Pseudo-first order model: \[ \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \] (5)

Linearized pseudo-second order model: \[ \frac{t}{q_t} = \frac{1}{q_e} + \frac{t}{k_2 q_e^2} \] (6)

Intraparticle diffusion model: \[ q_t = k_i t^{0.5} \] (7)

where \( q_t \) and \( q_e \) = amount of PO\textsubscript{4}-P adsorbed at time \( t \) and at equilibrium respectively (mg g\textsuperscript{-1}); \( k_1, K_2 \) and \( K_i \) = rate constants for pseudo-first order (min\textsuperscript{-1}), pseudo-second order (g mg\textsuperscript{-1} min\textsuperscript{-1}) and intra-particle diffusion (mg g\textsuperscript{-1} min\textsuperscript{-0.5}) models respectively (Ho and McKay 1998).

\( q_e \) values obtained from adsorption kinetics experiments were generally lower than batch adsorption \( q_e \) values and this may be due to some sample loss while taking solution aliquots periodically. Both pseudo-first order and intraparticle diffusion models gave very poor fits for most biochars compared to the linearized pseudo-second order model. \( R^2 \) values in the lattermost were higher and there was better agreement between experimental and calculated \( q_e \) values (Table 4). The pseudo-second order model has also been found to be a better fit for describing char dye sorption (Mahmoud et al. 2012). Intercept values were high in the intra-particle diffusion model and the regression plot not passing through the origin suggested that intra-particle diffusion was not a rate-controlling step (Cheung et al. 2007).

Conclusions

Effective phosphate recovery is important from environmental and socio-economic aspects as PO\textsubscript{4}-P is present in many types of wastewaters. This study was aimed at
investigating the potential for improving biochar phosphate adsorption capacities following chemical activation of biochars (post-treatment) and biomass (in-situ treatment) with metal salts, KOH and acids. In some cases, chemical treatment at low temperatures has been shown to improve biochar functionality somewhat. In terms of improving PO$_4$-P removal efficiency, biochars treated with magnesium salts were found to have a significant enhancement on the levels of PO$_4$-P adsorbed while other chemical activation methods improved PO$_4$-P adsorption marginally. Specifically, results showed that while untreated biochars adsorbed 0-4.4% phosphate, the treatment of oak and greenhouse waste improved phosphate adsorption from 3.6% to 70.3% in oak biochars, and from 2.1% to 66.4% in greenhouse waste biochars which compare favourably with other adsorbents.

Overall, findings from this study suggest that it is possible to enhance biochar phosphate adsorption capacity by treatment of biochars or biochar precursors (raw feedstock) with inorganic chemicals, albeit with more process optimization. Further research is also required to better understand why adsorbed PO$_4$-P release was minimal for most biochars, as this determines biochars' potential for reuse or for soil amendment.

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and may not in any circumstances be regarded as stating an official position of the
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Yorkshire, UK.

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doi:10.1016/0016-2361(86)90121-3


<table>
<thead>
<tr>
<th>Property</th>
<th>OAK 450</th>
<th>OAK 650</th>
<th>GHW 400</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%)</td>
<td>65.7</td>
<td>76.5</td>
<td>59.0</td>
</tr>
<tr>
<td>H (%)</td>
<td>2.7</td>
<td>1.4</td>
<td>2.9</td>
</tr>
<tr>
<td>N (%)</td>
<td>0.6</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>S (%)</td>
<td>0</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>O (%)</td>
<td>31.0</td>
<td>21.3</td>
<td>36.6</td>
</tr>
<tr>
<td>H/C</td>
<td>0.4</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>O/C</td>
<td>0.4</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>11.7</td>
<td>15.2</td>
<td>27.0</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>29.3</td>
<td>14.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>21.1</td>
<td>11.8</td>
<td>25.0</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>88.3</td>
<td>85.7</td>
<td>70.5</td>
</tr>
<tr>
<td>pH</td>
<td>9.9</td>
<td>10.3</td>
<td>10.6</td>
</tr>
<tr>
<td>BET surface area, N₂ (m² g⁻¹)</td>
<td>180.0</td>
<td>280.0</td>
<td>1.3</td>
</tr>
<tr>
<td>Total pore volume (cm³ g⁻¹)</td>
<td>0.150</td>
<td>0.160</td>
<td>0.003</td>
</tr>
<tr>
<td>P (%)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>K (%)</td>
<td>1.1</td>
<td>0.6</td>
<td>4.1</td>
</tr>
<tr>
<td>Ca (%)</td>
<td>4.4</td>
<td>5.0</td>
<td>3.6</td>
</tr>
<tr>
<td>Mg (%)</td>
<td>0.2</td>
<td>0.3</td>
<td>0.9</td>
</tr>
<tr>
<td>Na (%)</td>
<td>0.1</td>
<td>0.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*Oxygen content determined as difference between % C, H, N, S; elemental and mineral contents determined on dry basis (db).
Table 2. Elemental contents of some treated biochars

<table>
<thead>
<tr>
<th>Biochar</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>OAK 450 treated with KOH</td>
<td>74.1</td>
<td>3.2</td>
<td>0.5</td>
<td>0.02</td>
<td>22.2</td>
</tr>
<tr>
<td>OAK 650 treated with KOH</td>
<td>59.5</td>
<td>3.1</td>
<td>0.5</td>
<td>0.03</td>
<td>36.9</td>
</tr>
<tr>
<td>GHW 400 (surface) treated with KOH</td>
<td>70.3</td>
<td>4.0</td>
<td>0.9</td>
<td>0.05</td>
<td>24.8</td>
</tr>
<tr>
<td>OAK 450 treated with H$_2$O$_2$</td>
<td>71.3</td>
<td>3.9</td>
<td>0.5</td>
<td>0.00</td>
<td>24.3</td>
</tr>
<tr>
<td>OAK 650 treated with H$_2$O$_2$</td>
<td>63.7</td>
<td>2.3</td>
<td>0.5</td>
<td>0.00</td>
<td>33.3</td>
</tr>
<tr>
<td>GHW 400 treated with H$_2$O$_2$</td>
<td>68.8</td>
<td>4.6</td>
<td>0.9</td>
<td>0.46</td>
<td>25.2</td>
</tr>
<tr>
<td>OAK 450 treated with MgCl$_2$·6H$_2$O at 400 ºC</td>
<td>57.1</td>
<td>2.6</td>
<td>3.6</td>
<td>0.00</td>
<td>36.7</td>
</tr>
<tr>
<td>OAK 650 treated with MgCl$_2$·6H$_2$O at 600 ºC</td>
<td>65.1</td>
<td>1.8</td>
<td>0.7</td>
<td>0.11</td>
<td>32.3</td>
</tr>
<tr>
<td>Raw oak treated with MgCl$_2$·6H$_2$O at 600 ºC</td>
<td>53.6</td>
<td>2.5</td>
<td>0.3</td>
<td>0.20</td>
<td>43.5</td>
</tr>
<tr>
<td>Raw GHW treated with MgCl$_2$·6H$_2$O at 600 ºC</td>
<td>43.4</td>
<td>1.6</td>
<td>0.9</td>
<td>0.00</td>
<td>54.1</td>
</tr>
</tbody>
</table>

Carbon, hydrogen, nitrogen and sulphur contents expressed as % dry basis (db) and oxygen determined by difference between % C, H, N and S from 100.
Table 3. PO$_4$-P removal efficiencies of some adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Present study</th>
<th>Previous studies</th>
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<tbody>
<tr>
<td></td>
<td>PO$_4$-P adsorbed</td>
<td>PO$_4$-P adsorbed</td>
</tr>
<tr>
<td></td>
<td>(C$_0$ = 67 mg PO$_4^-$ L$^{-1}$)</td>
<td>(synthetic wastewater)$^#$</td>
</tr>
<tr>
<td></td>
<td>%  mg g$^{-1}$</td>
<td>%  mg g$^{-1}$</td>
</tr>
<tr>
<td>Oak 450 °C biochar</td>
<td>1.5  1.0±2.2</td>
<td>7.2  14.8±0.6</td>
</tr>
<tr>
<td>Oak 650 °C biochar</td>
<td>1   0.7±0.1</td>
<td>6.1  4.1±0.7</td>
</tr>
<tr>
<td>GHW 400 °C biochar</td>
<td>0   -2.2±0.2</td>
<td>0   -4.9</td>
</tr>
<tr>
<td>Mg oak biochar (in-situ)</td>
<td>95.9  64.6±0.2</td>
<td>&gt;95 &gt;64</td>
</tr>
<tr>
<td>Mg GHW biochar (in-situ)</td>
<td>96.5  65.1±1.3</td>
<td>&gt;95 &gt;64</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>La oak sawdust biochar (500°C)</td>
<td>~33</td>
</tr>
<tr>
<td>Fe (II) sugarcane bagasse fibre</td>
<td>97$^§$</td>
</tr>
<tr>
<td>MgO sugarcane bagasse biochar</td>
<td>&gt;35</td>
</tr>
<tr>
<td>MgO sugar beet tailing biochar</td>
<td>&gt;65</td>
</tr>
<tr>
<td>Digested sugar beet tailing biochar</td>
<td>&gt;70</td>
</tr>
<tr>
<td>Fe-Mn binary oxide</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Fe (II) activated carbon</td>
<td>~63 - 96$^§$</td>
</tr>
</tbody>
</table>

Synthetic wastewater concentrations (mg L$^{-1}$): SO$_4^{2-}$: 27.5 ± 0.5; NO$_2^-$: 46.4 ± 0.5; PO$_4^{3-}$: 67.4 ± 4.2; NO$_3^-$: 889.1 ± 7.3; Mg$^{2+}$: 28.6 ± 5.3; Ca$^{2+}$: 150.2 ± 0.6; Na$^+$: 318.7 ± 14.3; K$^+$: 513.5 ± 6.0; NH$_4^+$: 561.0 ± 5.4.

$^§$Initial PO$_4$-P concentrations of 11-46 mg L$^{-1}$; n.d.: not detected, thus total PO$_4$-P uptake assumed, although Mg$^{2+}$ present in synthetic wastewater may have contributed to PO$_4$-P removal.
### Table 4. Biochar PO$_4$-P adsorption kinetics model parameters for some biochars

<table>
<thead>
<tr>
<th>Biochar</th>
<th>$Q_{e \text{exp}}$</th>
<th>$Q_{e \text{cal}}$</th>
<th>$K_1$</th>
<th>$R^2$</th>
<th>$m$</th>
<th>$C$</th>
<th>$Q_{e \text{cal}}$</th>
<th>$k_2$</th>
<th>$R^2$</th>
<th>$k_i$</th>
<th>C</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OAK 450</td>
<td>24.08</td>
<td>0.000</td>
<td>1.2194</td>
<td>16.57</td>
<td>0.000</td>
<td>0.365</td>
<td>0.04</td>
<td>-4.15</td>
<td>-0.0005</td>
<td>0.965</td>
<td>0.05</td>
<td>38.08</td>
</tr>
<tr>
<td>OAK 650</td>
<td>24.14</td>
<td>0.000</td>
<td>1.516</td>
<td>32.81</td>
<td>0.000</td>
<td>0.656</td>
<td>0.05</td>
<td>-5.70</td>
<td>-0.0004</td>
<td>0.995</td>
<td>-0.31</td>
<td>50.94</td>
</tr>
<tr>
<td>GHW 400</td>
<td>16.57</td>
<td>0.000</td>
<td>0.6229</td>
<td>4.20</td>
<td>-0.001</td>
<td>0.037</td>
<td>0.07</td>
<td>15.72</td>
<td>15.1</td>
<td>0.0003</td>
<td>0.651</td>
<td>-0.52</td>
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<tr>
<td>OAK450-K</td>
<td>17.19</td>
<td>0.001</td>
<td>0.1726</td>
<td>1.49</td>
<td>-0.002</td>
<td>0.461</td>
<td>0.06</td>
<td>-5.08</td>
<td>16.1</td>
<td>-0.0008</td>
<td>0.994</td>
<td>-0.09</td>
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<tr>
<td>OAK650-K</td>
<td>25.86</td>
<td>0.000</td>
<td>0.9216</td>
<td>8.35</td>
<td>0.000</td>
<td>0.224</td>
<td>0.05</td>
<td>0.11</td>
<td>21.2</td>
<td>0.0198</td>
<td>0.984</td>
<td>0.41</td>
</tr>
<tr>
<td>GHW400-Ks</td>
<td>21.54</td>
<td>0.001</td>
<td>0.6585</td>
<td>4.56</td>
<td>-0.001</td>
<td>0.217</td>
<td>0.05</td>
<td>0.11</td>
<td>21.2</td>
<td>0.0198</td>
<td>0.984</td>
<td>0.11</td>
</tr>
<tr>
<td>OAK450-M</td>
<td>16.88</td>
<td>0.001</td>
<td>-0.199</td>
<td>0.63</td>
<td>-0.002</td>
<td>0.778</td>
<td>0.06</td>
<td>-10.45</td>
<td>15.6</td>
<td>-0.0004</td>
<td>0.974</td>
<td>-0.14</td>
</tr>
<tr>
<td>OAK650-M</td>
<td>101.79</td>
<td>0.000</td>
<td>1.9663</td>
<td>92.53</td>
<td>0.000</td>
<td>0.354</td>
<td>0.01</td>
<td>0.77</td>
<td>108.7</td>
<td>0.0001</td>
<td>0.991</td>
<td>4.21</td>
</tr>
<tr>
<td>OAK450-FC</td>
<td>16.56</td>
<td>0.003</td>
<td>0.7119</td>
<td>5.15</td>
<td>-0.007</td>
<td>0.399</td>
<td>0.06</td>
<td>-4.17</td>
<td>16.0</td>
<td>-0.0009</td>
<td>0.991</td>
<td>0.22</td>
</tr>
<tr>
<td>OAK650-FC</td>
<td>24.96</td>
<td>0.001</td>
<td>0.444</td>
<td>2.78</td>
<td>-0.001</td>
<td>0.768</td>
<td>0.04</td>
<td>-5.10</td>
<td>23.4</td>
<td>-0.0004</td>
<td>0.990</td>
<td>0.10</td>
</tr>
</tbody>
</table>

$Q_{e \text{exp}}$ and $Q_{e \text{cal}}$ = PO$_4$-P adsorbed determined from experiments and plots respectively (mg g$^{-1}$); $k_1$ (min$^{-1}$), $k_2$ (min g mg$^{-1}$) and $K_i$ (mg g$^{-1}$ min$^{-0.5}$) obtained from the respective plots of log($q_e$-$q_t$) versus $t$, $\frac{t}{q_t}$ versus $t$ and $q_t$ versus $t^{0.5}$; suffixes K and Ks refer to biochar treatment with KOH (chemical activation for oak biochars and surface activation for GHW); suffixes M and FC refer to chemical activation with MgCl$_2$·6H$_2$O and FeCl$_3$·6H$_2$O respectively.
Figure 1. CEC values of some treated and untreated biochars

Surface activation with: KOH (K_{SA}), \text{H}_2\text{O}_2; chemical activation involving pyrolysis with: \text{FeCl}_3\cdot6\text{H}_2\text{O} (FC), KOH (K_{CA}) and \text{MgCl}_2\cdot6\text{H}_2\text{O}
Figure 2. FTIR spectra of treated and untreated (a) OAK 450 (b) OAK 650 (c) GHW 400 biochars (K: KOH surface activation; H: $\text{H}_2\text{O}_2$ surface activation; Mg: chemical activation with $\text{MgCl}_2\cdot6\text{H}_2\text{O}$)
Figure 3. PO$_4$-P adsorption capacities of: (a) treated 450° C oak biochars; (b) treated 650° C oak biochars; (c) treated GHW 400° C biochars; (d) oak and greenhouse waste biomass treated with MgCl$_2$ and KOH at 600° C.