Phosphate and ammonium sorption capacity of biochar and hydrochar from different wastes

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Highlights

- PO₄-P adsorption capacity is more dependent on char calcium and magnesium content than on other ash components.
- NH₄-N adsorption capacity is a function of oxygen-containing functional groups, and physisorption is not the dominant mechanism for NH₄-N adsorption.
- Similarities in char sorption capacities regardless of processing conditions and feedstock.

Abstract

The potential for biochar and hydrochar to adsorb phosphate and ammonium is important for understanding the influence of these materials when added to soils, compost or other high nutrient containing environments. The influence of physicochemical properties such as mineral content, surface functionality, pH and cation exchange capacity has been investigated for a range of biochars and
hydrochars produced from waste-derived biomass feedstocks. Hydrochars produced from hydrothermal carbonisation at 250 °C have been compared to low and high temperature pyrolysis chars produced at 400-450 °C and 600-650 °C respectively for oak wood, presscake from anaerobic digestate (AD), treated municipal waste and greenhouse waste. In spite of differences in char physicochemical properties and processing conditions, PO$_4$-P and NH$_4$-N sorption capacities ranged from about 0-30 mg g$^{-1}$ and 105.8-146.4 mg g$^{-1}$ respectively. Chars with high surface areas did not possess better ammonium adsorption capacities than low surface area chars, which suggests that surface area is not the most important factor influencing char ammonium adsorption capacity, while char calcium and magnesium contents may influence phosphate adsorption. Desorption experiments only released a small fraction of adsorbed ammonium or phosphate (< 5 mg g$^{-1}$ and a maximum of 8.5 mg g$^{-1}$ respectively).

Keywords: Waste; Phosphate and Ammonium adsorption; Biochar; Hydrochar.

1. Introduction

Phosphate and ammonium recovery is important from an environmental management aspect as these species are contributors to eutrophication (Rittmann et al. 2011; Wang et al. 2015a; Zeng et al. 2013) and can be found in several wastewaters at varying concentrations (Bott et al. 2000; Barker et al. 2001; Battistoni et al. 2006; Cai et al. 2013; Grzmil and Wronkowski 2006; Song et al. 2011; Liu 2009; Ye et al. 2010). Ammonium makes up a very high proportion of soluble nitrogen in animal waste and can be adsorbed onto negatively-charged sites or between clay interlayers in soils (Fernando et al. 2005). When released however,
nitrifying bacteria convert this to nitrate in aerobic conditions which is eventually leached to groundwater (Fernando et al. 2005). Phosphate recovery is also important because an essential plant nutrient, there are growing concerns about its future availability (Rittmann et al. 2011). A number of ammonium and phosphate adsorbents have therefore been considered including chars obtained from the thermal treatment of organic matter in an oxygen-free atmosphere (biochars) or in the presence of subcritical water (hydrochars). Both biochars and hydrochars are heterogeneous structures comprised of carbonized organic matter, inorganic matter, sorbed volatiles and functional groups of nitrogen, sulphur and oxygen (Knicker 2007; Spokas et al. 2012). They are becoming increasingly attractive in a number of sectors as they can be derived from a wide range of waste biomass feedstocks and show potential as cost–effective, environmentally sustainable products for integrated waste management. Indeed, the application of biochars as adsorbents for soil nutrients, wastewater contaminants, pathogens and gases have been widely researched (Collison et al. 2009; Laird et al., 2010a; Spokas et al. 2012a; Wang et al. 2015a; Zeng et al. 2013; Zheng et al. 2010).

While several studies have highlighted positive, neutral and in some cases negative responses to biochar applications in a number of soils (Biederman and Harpole 2013; Spokas et al. 2012a; Uzoma et al. 2011), the mechanism by which chars adsorb nutrients and thus enhance soil productivity is not fully understood owing to variations in climate and soil. Furthermore, as char properties are a function of the nature of feedstocks used and biomass processing conditions (Collison et al. 2009; Wang et al. 2015a; Zhao et al. 2013), these variations further contribute to the challenges involved with quantifying their effect on nutrient cycling. Moreover, biochars influence nutrient cycling via biological, physical and chemical processes in
the short- and long-term (Laird et al. 2010a; Biederman and Harpole 2013). In the short-term, labile fractions of biochar and hydrochar may introduce bioavailable phosphorus and potassium to soils (Biederman and Harpole 2013; Laird et al. 2010b; Uzoma et al. 2011) as well as retain nutrient-rich soil water within their pores, while long-term biochar effects could involve creating favourable habitats for soil fungi such as mycorrhizae which influence nutrient cycling (Yamato et al. 2006). Chars may also increase soil alkalinity, resulting in an increase in phosphorus availability since at acidic conditions (pH < 4), this nutrient would be bound as insoluble iron and aluminium phosphates by aluminium and iron oxides respectively (Biederman and Harpole 2013; Uzoma et al. 2011; Xu et al. 2014). Char Cation Exchange Capacity (CEC) and surface chemistry could also influence nutrient retention (Laird et al. 2010a; Silber et al. 2010; Wang et al. 2015b); for instance, Zheng et al. (2010) observed that surface chemistry (negative surface charge) and metal-phosphate precipitation reactions played a more important role than surface area in the ammonium and phosphate sorption capacities respectively. Indeed, Borchard et al. (2012) noted that only specific types of biochars can improve soil nutrient retention, aggregation and CEC, and that these biochars tend to possess hydrophilic surfaces. It is hypothesised that biochar produced at lower temperatures may have better ammonium adsorption capacity due to the presence of increased negatively-charged functional groups like carboxylates (Liang et al. 2006), and a positive relationship has been observed between biochar CEC, surface area and ammonium sorption (Zeng et al. 2013). Conversely, biochar phosphate adsorption capacity is thought to increase with increasing levels of metal ions, thus biochars with lower ash content will have lower phosphate adsorption capacities.
The objectives of this work were therefore to: (i) investigate the potential for phosphate and ammonium recovery by biochars and hydrochars produced from various feedstocks; (ii) investigate the influence of physicochemical properties including elemental content, mineral content and surface functionality on nutrient sorption and adsorption mechanisms. Overall, this work was aimed at promoting a better understanding of the interaction of nutrients with biochars and hydrochars and how this may impact their application.

2. Methods

2.1 Materials

A set of five feedstock have been used in this study: oak wood and greenhouse waste sourced from Andalucia, Spain; Anaerobically Digested (AD) waste sourced from Organic Waste Systems (OWS), Belgium; treated municipal waste sourced from Graphite resources, UK. Chemicals for various analyses were used as received.

2.2 Biochar and hydrochar production

Samples of biochar were produced by Energy research Centre of the Netherlands (ECN) at 400 °C and 600 °C using a screw thread Pyromaat reactor. Pyrolysis chars were also supplied by a commercial pyrolysis plant operated by Proininso, Spain. Hydrochars were produced at the University of Leeds using a 500 mL stainless steel Parr 4836 reactor. Hydrothermal Carbonization (HTC) experiments were performed using 10 wt. % solids/water slurries at 250 °C for 1 h at approximately 4 MPa following which the hydrochars were filtered and air-dried.
2.3 Biochar and hydrochar characterisation

2.3.1 Agronomical analyses

Ultimate analyses of biochar and hydrochar samples were determined using a CHN Elemental Analyser (Thermo Scientific Flash 2000). Proximate analysis was performed in a muffle furnace following the BS method for biomass. 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 (Perkin Elmer) following digestion in nitric acid. pH measurements were made after 1:20 char/distilled water mixtures were shaken and allowed to stand for 2 h. Solvent extraction of chars was performed by exhaustive soxhlet extraction at room temperature using toluene. Solid state NMR has been performed in cross-polarisation mode on a Bruker Avance III HD for chars from Oak wood by hydrothermal carbonisation at 250°C and pyrolysis at 400°C and 600°C. This facility is operated by the University of Durham, EPSRC facility.

CEC was determined using a method similar to that of Brewer (2012), Gaskin et al. (2008) and Yuan et al. (2011). 20 mL distilled water was added to 1g of biochar and shaken at 160 rpm for 10 minutes 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 1M sodium acetate (Alfa Aesar) with pH adjusted to 7 using a few drops of glacial acetic acid, shaken at 160 rpm for 16 minutes and filtered. This was repeated twice more, discarding the leachates each time, after which biochars were rinsed with ethanol (Fischer Scientific UK) thrice for 8 minutes each at 160 rpm. Three additions of 1M ammonium acetate (Fischer Scientific UK) at pH 7 were used to displace sodium cations by shaking at 160 rpm for 16 minutes, storing the
leachates for subsequent analysis. Analyses were done in duplicate or triplicate, 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.

2.4 Phosphate and ammonium adsorption capacity

2.4.1 Batch adsorption

All containers were acid washed with 1 M HCl and rinsed with deionised water before use. 0.1 g biochar (≤850 µm) was transferred to plastic Nalgene containers and 100 mL of 125 mg P L⁻¹ phosphate solution prepared from potassium phosphate monobasic (Fischer Scientific UK) was added after its pH was adjusted to 7 with 1 M NaOH. The containers were tightly sealed and shaken at 160 rpm for 24 h in a water shaker bath (SW23 Julabo GmbH) at room temperature. 10mL aliquots of each sample were taken after 24 h and filtered through 0.45 µm Sartorius Minisart syringe filters for Ion Chromatography analysis (Metrohm 850 Professional IC–AnCat). This procedure was repeated for ammonium solutions, using about 1000 mg NH₄⁺–L⁻¹ prepared from ammonium chloride (Fischer Scientific UK). Most analyses were done in duplicate and the average values reported. The concentrations of adsorbed ions were determined as:

\[ q_e = \frac{(C_o - C_e)V}{M} \]  

where \( C_o \) and \( C_e \) = initial and equilibrium liquid-phase phosphate or ammonium adsorbate concentrations respectively (mg L⁻¹); \( V \) = volume of solution (L); \( M \) = mass of char (g).
2.4.2 Desorption isotherms

Adsorbed phosphate and ammonium in chars were extracted using a similar procedure as outlined above but using 0.01 M KCl solution. 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 and ammonium adsorption mechanisms, 0.1 g chars (≤850µm) were each added to 125 mg P L\(^{-1}\) or 1000 mg NH\(_4^+\) L\(^{-1}\) solutions respectively, 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. Samples were filtered, analysed by Ion Chromatography and the concentration of adsorbed ions were determined.

2.4.4 Adsorption isotherms at varying initial concentrations

0.1 g of char with highest carbon contents (oak and greenhouse waste) was added to varying concentrations of phosphate solutions, specifically 50-200 mg P L\(^{-1}\), and ammonium concentrations ranging from about 360-815 mg NH\(_4^+\) L\(^{-1}\). These concentrations were chosen to represent some real-case wastewater concentrations. The mixtures were shaken at 160 rpm for 24 h at room temperature, keeping all other parameters identical to batch adsorption tests. Samples were filtered, analysed by Ion Chromatography and the concentration of adsorbed ions were determined as in Section 2.4.1.
3. Results and Discussion

3.1 Effect of pyrolysis on biochar physicochemical properties

As pyrolysis temperature increases, carbon content predictably increases as shown in Table 1. Volatile matter was generally higher in hydrochars while ash contents were comparable in both hydro- and bio-chars. Oak chars generally had lower ash contents compared to waste chars, which is likely why carbon contents in the former were higher; wood chars are known to possess higher cellulose and hemicellulose contents which carbonize during pyrolysis (Kizito et al. 2015). Biochar pH values were alkaline, ranging from 8.6-11.1 while hydrochars were mostly acidic, ranging from 4.8-7.2. In accordance with European Biochar Certificate requirements for biochars intended for soil amendment (IBI 2014), carbon contents were > 50% dry mass for greenhouse waste chars and both oak chars, O/C ratios were < 0.4 in all chars except 400°C municipal waste biochar and H/C ratios were < 0.7 in all but 4 chars (hydrochars of presscake, greenhouse waste, municipal waste and 400°C municipal waste biochars). Both oak wood samples exhibited similar physicochemical characteristics, both possessing the highest carbon contents. Calcium and magnesium contents were generally higher than the other macro-minerals (Table 2); the former ranged from 1.6-8.1% and increased with pyrolysis temperature while magnesium contents ranged from 0-1.2%, with most biochars possessing 0.2-0.5%.
3.2 Biochar and hydrochar CEC

CEC is known to decrease with an increase in pyrolysis temperature (Lehmann 2007; Silber et al. 2010), but only non-commercial oak chars (OW) exhibited this trend (Table 2). Higher temperature biochars (600-650°C) generally had higher CEC than lower temperature biochars (400-450°C). Regardless of their higher oxygen contents, hydrochar CEC values were generally lower than biochar CEC, however, positive correlations between bio- and hydro-char oxygen content and CEC were found ($\rho_{X,Y} = 0.8$) as expected (Wang et al. 2015b). No relationship between char CEC and surface area was evident; for instance, the CEC of 450°C commercial oak and 400°C presscake biochars were similar despite marked differences in surface area (180 m² g⁻¹ and 2 m² g⁻¹ respectively). The results indicate that oak and greenhouse waste typically produce a higher CEC than the municipal waste and presscake biochars possibly because these feedstocks contain higher lignocellulosic contents and lower ash contents.

To better understand the CEC trends, CEC measurements were performed on chars following solvent extraction in toluene compared with as-received chars. Solvent extraction had different effects on the two types of char: in hydrochars, the CEC in most cases improved (Fig. 1(a)); in biochars, the CEC remained unchanged or decreased after solvent extraction, the latter more prevalent for the higher temperature biochars (Fig. 1(c)). As CEC is said to be a function of surface area and functionality, an increase in hydrochar CEC following solvent extraction could suggest either the unblocking of pores increasing porosity and surface area, or that a higher surface functionality is being revealed by removing tars. The latter effect may be more important as surface area had negligible influence on char CEC, with hydrochars possessing low surface areas (< 6 m² g⁻¹). Based on the assumption that
carboxyl and other functional groups improve CEC (Boehm 1994; Glaser et al. 2002; Warner 1977), the removal of volatile hydrocarbons from the surface of the biochar containing these groups by solvent extraction is expected to affect CEC by revealing a different surface functionality below.

Table 1. Char physicochemical properties

<table>
<thead>
<tr>
<th>Biochar</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O† (%)</th>
<th>Ash content (%)</th>
<th>Volatile matter (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250°C hydrochars</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oak wood</td>
<td>67.9</td>
<td>6.5</td>
<td>1.4</td>
<td>18.8</td>
<td>6.2</td>
<td>6.2</td>
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<tr>
<td>Greenhouse waste</td>
<td>66.4</td>
<td>6.8</td>
<td>3.1</td>
<td>18.3</td>
<td>5.2</td>
<td>61.6</td>
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<td>45.2</td>
<td>6.0</td>
<td>2.0</td>
<td>8.6</td>
<td>38.0</td>
<td>42.8</td>
</tr>
<tr>
<td>Presscake from AD</td>
<td>22.8</td>
<td>2.0</td>
<td>0.9</td>
<td>4.5</td>
<td>69.8</td>
<td>20.7</td>
</tr>
<tr>
<td>400-450°C biochars</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Oak wood (commercial)</td>
<td>65.7</td>
<td>2.7</td>
<td>0.6</td>
<td>8.9</td>
<td>11.7</td>
<td>21.1</td>
</tr>
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<td>Oak wood</td>
<td>70.9</td>
<td>3.6</td>
<td>0.4</td>
<td>12.9</td>
<td>12.1</td>
<td>20.8</td>
</tr>
<tr>
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<td>59.0</td>
<td>2.9</td>
<td>1.2</td>
<td>9.6</td>
<td>27.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Municipal waste</td>
<td>39.9</td>
<td>3.7</td>
<td>1.7</td>
<td>4.2</td>
<td>50.1</td>
<td>26.2</td>
</tr>
<tr>
<td>Presscake from AD</td>
<td>17.1</td>
<td>0.8</td>
<td>0.9</td>
<td>1.5</td>
<td>79.5</td>
<td>13.4</td>
</tr>
<tr>
<td>600-650°C biochars</td>
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<td></td>
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<tr>
<td>Oak wood (commercial)</td>
<td>76.5</td>
<td>1.4</td>
<td>0.8</td>
<td>7.0</td>
<td>14.3</td>
<td>11.8</td>
</tr>
<tr>
<td>Oak wood</td>
<td>79.2</td>
<td>2.0</td>
<td>0.3</td>
<td>3.5</td>
<td>13.4</td>
<td>9.2</td>
</tr>
<tr>
<td>Greenhouse waste</td>
<td>63.0</td>
<td>1.2</td>
<td>0.9</td>
<td>7.5</td>
<td>17.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Municipal waste</td>
<td>40.1</td>
<td>1.1</td>
<td>1.4</td>
<td>3.2</td>
<td>53.8</td>
<td>18.7</td>
</tr>
<tr>
<td>Presscake from AD</td>
<td>18.5</td>
<td>0.5</td>
<td>0.6</td>
<td>0.0</td>
<td>83.4</td>
<td>7.6</td>
</tr>
</tbody>
</table>

†O content determined by difference.
<table>
<thead>
<tr>
<th>Biochar</th>
<th>pH</th>
<th>CEC</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
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<tr>
<td></td>
<td></td>
<td>(cmol(_c)·kg(^{-1}))</td>
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<tr>
<td><strong>250 °C hydrochars</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Oak wood</td>
<td>4.8</td>
<td>88.3 ± 9.7</td>
<td>1000</td>
<td>0</td>
<td>23,000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Greenhouse waste</td>
<td>5.8</td>
<td>83.1 ± 19.4</td>
<td>2000</td>
<td>7000</td>
<td>16,000</td>
<td>2000</td>
<td>0</td>
</tr>
<tr>
<td>Municipal waste</td>
<td>6.2</td>
<td>44.5 ± 1.7</td>
<td>3000</td>
<td>9000</td>
<td>24,000</td>
<td>4000</td>
<td>0</td>
</tr>
<tr>
<td>Presscake from AD</td>
<td>7.2</td>
<td>62.6 ± 3.5</td>
<td>5000</td>
<td>2000</td>
<td>27,000</td>
<td>6000</td>
<td>300</td>
</tr>
<tr>
<td><strong>400-450 °C biochars</strong></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Oak wood (commercial)</td>
<td>9.9</td>
<td>59.4 ± 8.1</td>
<td>2000</td>
<td>11,000</td>
<td>44,000</td>
<td>2000</td>
<td>1000</td>
</tr>
<tr>
<td>Oak wood</td>
<td>9.7</td>
<td>105.8 ± 12.1</td>
<td>1000</td>
<td>9000</td>
<td>27,000</td>
<td>2000</td>
<td>1000</td>
</tr>
<tr>
<td>Greenhouse waste</td>
<td>10.6</td>
<td>109.5 ± 21.8</td>
<td>4000</td>
<td>41,000</td>
<td>36,000</td>
<td>9000</td>
<td>4000</td>
</tr>
<tr>
<td>Municipal waste</td>
<td>9.5</td>
<td>65.7 ± 16.2</td>
<td>5000</td>
<td>9000</td>
<td>53,000</td>
<td>5000</td>
<td>8000</td>
</tr>
<tr>
<td>Presscake from AD</td>
<td>10.3</td>
<td>51.0 ± 5.5</td>
<td>6000</td>
<td>12000</td>
<td>39,000</td>
<td>6000</td>
<td>4000</td>
</tr>
<tr>
<td><strong>600-650 °C biochars</strong></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Oak wood (commercial)</td>
<td>10.3</td>
<td>76.6 ± 0.7</td>
<td>2000</td>
<td>6000</td>
<td>50,000</td>
<td>3000</td>
<td>0</td>
</tr>
<tr>
<td>Oak wood</td>
<td>8.6</td>
<td>65.2 ± 20.2</td>
<td>1000</td>
<td>2000</td>
<td>3100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Greenhouse waste</td>
<td>11.0</td>
<td>146.2 ± 32.3</td>
<td>4000</td>
<td>50,000</td>
<td>45,000</td>
<td>12,000</td>
<td>4000</td>
</tr>
<tr>
<td>Municipal waste</td>
<td>10.2</td>
<td>67.9 ± 12.5</td>
<td>5000</td>
<td>9000</td>
<td>81,000</td>
<td>5000</td>
<td>14,000</td>
</tr>
<tr>
<td>Presscake from AD</td>
<td>10.1</td>
<td>52.6 ± 11.5</td>
<td>5000</td>
<td>11,000</td>
<td>36,000</td>
<td>5000</td>
<td>4000</td>
</tr>
</tbody>
</table>

Mineral contents determined on dry basis (db) and reported in ppm.

Biochar CEC was generally similar before and after extraction but for the 600-650 °C biochars, CEC was slightly higher for the as-received biochars indicating that solvent extraction reduced their surface functionality. There are some anomalies observed in 400 °C oak biochar, but the general emerging trend shows that hydrochar CEC is enhanced after extraction while biochars are either unaffected or lowered after extraction. This provides supporting evidence that CEC is potentially higher for hydrochar but the levels of tars on its surface affect its CEC. Indeed, water-insoluble fatty acids were found sorbed onto hydrochars produced from
microalgae (Heilmann et al. 2011) and brewer’s spent grain (Poerschmann et al. 2015), based on analyses with ether and chloroform/methanol solvents respectively. In this study, NMR analysis of chars confirmed that the surface functionality of low and high temperature chars differed considerably, with high temperature biochars possessing fewer functional groups (Supplemental Fig. A1). Extracts analysed by GC-MS also confirmed the removal of oxygenated groups and hydrocarbons from hydrochars and biochars respectively (data not included).

Figure 1. Effect of solvent extraction on biochar CEC
MW: municipal waste; GH: greenhouse waste; PK: presscake
CEC_{ar} and CEC_{sox} refer to CEC before and after solvent extraction respectively
3.3 Char PO$_4$-P adsorption

PO$_4$-P concentrations in various wastewaters can range from <14 mg L$^{-1}$ to over 15,000 mg L$^{-1}$ (Battistoni et al. 2006; Cai et al. 2013; Grzmil and Wronkowski 2006). In this study, PO$_4$-P at initial concentrations of about 400 mg PO$_4^{3-}$ L$^{-1}$ were used, and char PO$_4$-P sorption capacities are presented in Table 3. Most results had coefficients of variation <5% but greenhouse waste samples consistently showed much higher percent variations, likely due to sample heterogeneity. PO$_4$-P release occurred in greenhouse waste and presscake hydrochars and 450°C commercial oak biochar, and such release has also been observed in low and high temperature biochars elsewhere (Zeng et al. 2013). PO$_4$-P release does not appear to be due to char P content, as water extraction of chars using a similar procedure as outlined in Section 2.4.1 showed that oak hydrochars and commercial oak biochars produced at 450°C and 650°C respectively released 1.18 ± 0.04, 0.554 ± 0.003 and 1.19 ± 0.03 mg g$^{-1}$ PO$_4$-P while greenhouse waste biochars produced at 400°C and 600°C released 2.1 ± 0.1 and 3.5 ± 0.2 mg g$^{-1}$ PO$_4$-P respectively. On the other hand, char P might not always be completely extractable with concentrated acid (Mukherjee and Zimmerman 2013) or by water.

The PO$_4$-P adsorption capacities of oak and greenhouse waste chars were compared at varying initial concentrations as shown in Figs. 2(a)-(b). PO$_4$-P adsorption improved with increasing initial concentration possibly due to higher concentration gradients, resulting in better filling of reactive adsorption sites (Chen et al. 2013; Krishnan and Haridas 2008; Wang et al. 2011; Xue et al. 2009). However, Chen et al. (2013) and Wang et al. (2011) found that while phosphate adsorption increased with initial concentration, adsorption efficiency (i.e. removal ratio) decreased possibly because of fewer active adsorption sites available at higher initial
PO₄-P concentrations. This was also the case for chars in this study, with adsorption efficiencies highest at 170 mg PO₄-P L⁻¹ in most cases. While pyrolysis temperature and feedstock composition variation did not affect char adsorption capacity substantially, hydrochars generally exhibited lower adsorption capacities.

Linearized Langmuir isotherm models did not fit the data for any of the chars and the linearized Freundlich isotherm model described the adsorption mechanism slightly better, based on $R^2$ values and a better agreement between experimental and calculated $q_e$ values. The Freundlich model is said to suit phosphate sorption better because as adsorbents become saturated, adsorption affinity decreases exponentially (Sakadevan and Bavor 1998) or because of precipitation reactions (Zeng et al. 2013). Conversely, the Langmuir model fitted better than Freundlich model in Wang et al. (2011) and Zeng et al. (2013), possibly resulting from the effect of biochar P release (Zeng et al. 2013). In this study, adsorption intensity ($n$) > 1 suggested positive adsorption in oak biochars and 400°C greenhouse waste biochars.

Linearized Langmuir isotherm (Type II):
$$\frac{1}{q_e} = \left(\frac{1}{k_a q_m}\right) \frac{1}{C_e} + \frac{1}{q_m}$$  (2)

Linearized Freundlich isotherm:
$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  (3)

where $q_e$ and $q_m$ = amount of species adsorbed at equilibrium and saturated monolayer adsorption respectively (mg g⁻¹), $C_e$ = equilibrium concentration (mg L⁻¹), $n$ = adsorption intensity, $k_a$ and $K_F$ = Langmuir and Freundlich constants respectively (Ho 2004; Kumar and Sivanesan 2007).
Table 3. Char PO₄-P and NH₄-N sorption capacity

| Biochar                  | PO₄-P | | NH₄-N | |
|--------------------------|-------|--------------------------|
|                          | qₑ    | % PO₄⁺⁻ ads. | Kᵤ (mg g⁻¹) | Desorbed | qₑ    | % NH₄-N ads. | Kᵤ (mg g⁻¹) | Desorbed | Desorbability |
| 250°C hydrochars         |       |              |              |          |       |              |              |          |               |
| Oak wood                 | 26.6 ± 10.3 | 6 | 0.07 | n.d | 109.7 ± 14.1 | 12 | 0.12 | n.d | 0 |
| Greenhouse waste         | -9.6 ± 7.6  | 0 | -0.02 | n.d | 121.7 ± 0.3  | 13 | 0.13 | 4.8 | 0.03 |
| Municipal waste          | 5.1 ± 3.8   | 1 | 0.01 | n.d | 146.4 ± 5.8   | 14 | 0.16 | 4.0 | 0.03 |
| Presscake from AD        | 37.0 ± 7.1  | 9 | 0.10 | n.d | 129.0 ± 19.5  | 17 | 0.16 | 4.2 | 0.03 |
| 400-450°C biochars       |       |              |              |          |       |              |              |          |               |
| Oak wood (commercial)    | -0.3 ± 6.1  | 0 | -0.001 | n.d | 100.9 ± 3.4  | 9 | 0.11 | 5.0 | 0.05 |
| Oak wood                 | 5.5 ± 19.0 | 1 | 0.01 | n.d | 129.4 ± 34.8 | 13 | 0.11 | 5.0 | 0.05 |
| Greenhouse waste         | 18.7 ± 1.9  | 4 | 0.05 | n.d | 118.2 ± 26.9 | 12 | 0.13 | 4.8 | 0.04 |
| Municipal waste          | 11.9 ± 4.3 | 3 | 0.03 | n.d | 137.3 ± 0.6  | 13 | 0.15 | 3.0 | 0.02 |
| Presscake from AD        | 7.8 ± 1.4  | 2 | 0.018 | n.d | 105.8 ± 11.5 | 9 | 0.11 | 4.0 | 0.04 |
| 600-650°C biochars       |       |              |              |          |       |              |              |          |               |
| Oak wood (commercial)    | 15.1 ± 5.9 | 4 | 0.04 | n.d | 114.4 ± 3.4  | 11 | 0.12 | 5.0 | 0.04 |
| Oak wood                 | 3.6 ± 6.1 | 1 | 0.01 | n.d | 123.5 ± 28.7 | 12 | 0.16 | n.d | 0 |
| Greenhouse waste         | 9.1 ± 6.5  | 2 | 0.02 | 8.5 | 99.3 ± 28.5  | 10 | 0.11 | n.d | 0 |
| Municipal waste          | 14.3 ± 0.6 | 4 | 0.04 | n.d | 128.3 ± 6.7  | 13 | 0.14 | 2.8 | 0.02 |
| Presscake from AD        | 30.0 ± 24.9| 7 | 0.08 | n.d | 136.2 ± 18.1 | 13 | 0.15 | 2.2 | 0.02 |

Phosphate C₀ ≈ 400 mg L⁻¹; ammonium C₀ ≈ 1000 mg L⁻¹; n.d: not detected; desorbability = ratio of NH₄-N desorbed to NH₄-N adsorbed.
PO₄-P adsorption was highest a few hours after sorption tests began with the exception of 600°C greenhouse waste biochar (Supplemental Fig. A2). This is contrary to other studies, which observed adsorption equilibrium concentrations after 24 h at room temperature (Wang et al. 2011; Zhang et al. 2012). This might be due to the higher PO₄-P concentration used in this study. Oak char kinetics followed a more predictable pattern than greenhouse waste biochars, and based on linear regression analysis, the pseudo-second order model provided the best fit.

3.4 Possible reaction mechanisms for biochar PO₄-P sorption

PO₄-P sorption mechanisms are thought to be dependent on metal ion reactions (precipitation, surface deposition), surface area and surface functionality (Wang et al. 2015a; Yao et al. 2013; Zeng et al. 2013). The influence of biochar surface area on PO₄-P adsorption is unclear but some studies suggest that its influence may be minor compared to adsorbent elemental composition. Wang et al. (2015a) for instance found that the best performing biochars did not possess superior surface areas compared to other biochars. Previous studies have also suggested that since biochars tend to be negatively charged, surface functionality may not influence phosphate sorption a great deal (Yao et al. 2011; Zeng et al. 2013).

In this study, PO₄-P sorption capacity increased with pyrolysis temperature, with the exception of commercial oak and greenhouse waste biochars (Fig. 3). This is in agreement with findings of Wang et al. (2015a) who observed an increase in PO₄-P adsorption with pyrolysis temperature up to a certain point (500°C). Generally, char PO₄-P sorption capacities in this study were found to be lower than other adsorbents, but some positive correlation between PO₄-P adsorption and Ca or Mg contents were observed in hydrochars and biochars, and to a lesser degree with ash content. Xue et al. (2009) also found that adsorbent chemical composition was most
influential, leading to simultaneous chemical precipitation and ligand exchange between adsorbent and $\text{PO}_4^-\text{P}$. Furthermore, Yao et al. (2011) compared biochars produced from raw and from anaerobically digested sugar beet tailings and found that $\text{PO}_4^-\text{P}$ adsorption capacities increased in the latter biochars possibly due to the presence of surface MgO as this compound was absent in the former. Other cations including $\text{Ca}^{2+}$, $\text{Al}^{3+}$ and La are known to improve phosphate adsorption as well (Wang et al. 2015a; Xue et al. 2009; Yao et al. 2013; Zeng et al. 2013), particularly if they are present as basic functional groups. Wang et al. (2015a) for instance observed that biochar $\text{PO}_4^-\text{P}$ adsorption capacity was a function of ketones, pyrones and chromens based on a positive correlation of these groups with $\text{PO}_4^-\text{P}$ removal efficiency, although $R^2$ values of 0.73 suggested that these groups were not solely responsible.

$\text{PO}_4^-\text{P}$ desorption from chars in this study was minimal, hence $\text{PO}_4^-\text{P}$ desorbability, described by Xue et al. (2009) and Ye et al. (2006) as a ratio of desorbed phosphate to total adsorbed phosphate, could not be determined in all but 2 biochars. Low $\text{PO}_4^-\text{P}$ desorption might have been because $\text{PO}_4^-\text{P}$ ions were strongly bound to the chars or because the extracting solution was inadequate. As easily desorbed phosphates may be indicative of physical adsorption rather than chemical adsorption (Xue et al. 2009), the former might be more likely. Xue et al. (2009) and Ye et al. (2006) also found that basic oxygen furnace slag and palygorskite adsorbents respectively did not desorb a lot of phosphate regardless of initial phosphate concentration although desorbability increased to some extent with an increase in amount of adsorbed phosphate.
Figure 2. Effect of increasing $\text{PO}_4^2-$P and $\text{NH}_4$-N concentration on sorption on oak and greenhouse waste chars.
Data fitted to kinetic models showed that the pseudo-second order model consistently gave a closer fit compared to the pseudo-first order and intra-particle diffusion models. While the latter two models gave average $R^2$ values of 0.53 and 0.28 respectively, the pseudo-second order $R^2$ values were higher (Supplemental Table A1). Previous studies have also observed many metals and heavy elements follow this pattern (Limousin et al. 2007). Wang et al. (2011) also found this model fitted better than the intra-particle diffusion model. Based on their adsorption kinetics data, simultaneous rapid surface adsorption of PO$_4$-P and slower intra-particle diffusion through the adsorbent occurred simultaneously.

Solvent extraction had variable effects on char PO$_4$-P adsorption (Fig. 3). PO$_4$-P adsorption improved in some low temperature biochars (400-450°C); 400°C oak biochar which released phosphate into solution prior to extraction performed marginally better after extraction. For 600-650°C biochars, solvent extraction decreased % PO$_4$-P adsorption however. These did not appear to be related to volatile matter, ash content or elemental composition.
Figure 3. Comparison of PO₄-P adsorption capacities of solvent extracted and non-extracted chars
PK: presscake; MW: municipal waste; CO: commercial oak; GH: greenhouse waste; OW: oak wood biochars solvent extracted chars are denoted ‘sox’
3.5 Char NH₄-N sorption

Previous studies have shown that pH, time and initial NH₄⁺ concentrations are important factors that determine biochar adsorption capacity (Fernando et al. 2005; Kizito et al. 2015; Schlegel et al. 1999). NH₄-N adsorption increased at higher initial solution concentrations but only to a certain point for oak hydrochar and 600°C greenhouse waste biochar (Figs. 2(c)-(d)). Preliminary results showed that many biochars released, rather than adsorbed NH₄-N at initial concentrations below 400 mg L⁻¹ (data not included). However, this may not be resulting from the lower initial concentration since biochars are capable of adsorbing NH₄-N at low concentrations. Subsequent adsorption tests with untreated biochars were however performed at a higher initial concentration of about 1000 mg NH₄⁺ L⁻¹ and presented in Table 3. NH₄-N adsorption data were fitted to the linearized Langmuir and Freundlich isotherm models, and although not an optimal fit, the Langmuir isotherm model described ammonium adsorption better, based on higher $R^2$ values (0.75-0.91 for commercial oak chars and 0.91 for greenhouse waste 250°C and 600°C). As observed in char PO₄-P sorption, the pseudo-second order model generally had higher $R^2$ values (Table 5) compared to the pseudo-first order and intra-particle diffusion models, although not an optimal fit in many cases.

Desorption of NH₄-N after KCl extraction was minimal and this has been observed elsewhere (Clough et al. 2013; Fernando et al. 2005; Saleh et al. 2012). This might have been because NH₄-N was effectively trapped within the biochar pore structure, because the salt solution (KCl) was not effective in extracting adsorbed NH₄-N (Saleh et al. 2012), or due to NH₃-N volatilization especially for high pH biochars (Wang et al. 2015b).
3.6 Possible reaction mechanisms for NH$_4^+$ sorption

NH$_4$-N adsorption was marginally higher in most lower temperature biochars and hydrochars. This general decrease in NH$_4$-N adsorption with temperature is expected, and Zeng et al. (2013) noted that the absence of aromatic C=O and C=C, -CH$_2$-, CO and CC functional groups from a high temperature biochar (600°C) after NH$_4$-N adsorption suggested that these functional groups reacted with NH$_4$-N. A positive relationship between biochar acid functional groups and NH$_4$-N adsorption was observed in Wang et al. (2015a), which corroborated earlier speculations by Zheng et al. (2010) that with increasing pyrolysis temperature, NH$_4$-N sorption decreased due to loss of biochar polar groups.

In terms of nutrient adsorption, it is becoming increasingly apparent that char surface groups may play a more important role than surface area and porosity in both biochars and hydrochars (Bargmann et al. 2014; Spokas et al. 2012). Preliminary studies on municipal waste and presscake biochars pyrolysed in 1% oxygen also showed improved NH$_4$-N adsorption capacities (data not included). As observed in char CEC, a positive relationship between oxygen content and NH$_4$-N was observed following solvent-extraction (Fig 4). Presscake and commercial oak biochars possessed similar NH$_4$-N adsorption capacities in spite of very different surface areas (2.5 m$^2$ g$^{-1}$ and 280 m$^2$ g$^{-1}$ respectively), suggesting that physisorption/ion exchange might not be the dominant mechanism by which NH$_4$-N adsorption occurred. Liang et al. (2006) also noted that high O/C ratios could be responsible for nutrient adsorption since potassium to carbon ratios were at least 0.18 higher at black carbon surfaces than at interior portions.

NH$_4$-N adsorption onto soluble organic matter on char surfaces has also been suggested as a possible process, based on observations of increased NH$_4$-N
adsorption in complex solutions (dairy or swine effluents) compared to simple solutions (ammonium chloride) (Fernando et al. 2005; Sarkhot et al. 2013), although the reverse effect has also been observed, as in Kizito et al. (2015). No clear trends were observed between char organic matter content and NH$_4$-N adsorption capacity in this study.
Figure 4. Comparison of NH$_4^+$-N adsorption capacities of solvent extracted and non-extracted chars showing variable trends; solvent extracted chars denoted by prefix ‘S’.

GH: greenhouse waste; MW: municipal waste; CO: commercial oak; OW: oak wood; PK: presscake biochars
Conclusions

This study investigated the phosphate and ammonium adsorption capacities of biochars derived from various waste biomass feed-stocks, comparing key physicochemical properties such as surface area, CEC, ash and mineral content. Solvent extraction improved hydrochar CEC, possibly due to removal of hydrophobic compounds. Conversely, slow pyrolysis biochar CEC generally decreased following solvent extraction.

Char PO$_4^-$P and NH$_4^+$-N sorption capacities ranged from about 0-30 mg g$^{-1}$ and 105.8-146.4 mg g$^{-1}$ respectively with generally low desorption of both ions. Biochar phosphate adsorption capacity increased with pyrolysis temperature, possibly due to metal ion precipitation reactions between phosphate and char calcium and magnesium. In contrast, a positive relationship between char oxygen functional groups, CEC and NH$_4^+$-N adsorption suggested that NH$_4^+$-N adsorption may have occurred mainly via chemical reactions with oxygen-containing functional groups rather than ion-exchange/physisorption. Overall however, in spite of differences in physicochemical properties and processing conditions, there was no great variation in char phosphate and ammonium sorption capacities between the chars.

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