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

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Highlights

- PO_4-P adsorption capacity is more dependent on char calcium and magnesium content than on other ash components.
- NH_4-N adsorption capacity is a function of oxygen-containing functional groups, and physisorption is not the dominant mechanism for NH_4-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℃ and 600℃ 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℃ 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℃ and pyrolysis at 400℃ and 600℃. 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 1 M 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 NH_4^+-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:

$$q_e = (C_o - C_e)\frac{V}{M} \qquad (1)$$

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).

168 2.4.2 Desorption isotherms

169 Adsorbed phosphate and ammonium in chars were extracted using a similar
170 procedure as outlined above but using 0.01 M KCl solution. 10 mL aliquots of each
171 sample were taken after 24 h then filtered through 0.45 µm Sartorius Minisart syringe
172 filters for Ion Chromatography analysis.

173 2.4.3 Adsorption kinetics

174 To investigate possible phosphate and ammonium adsorption mechanisms, 0.1 g
175 chars (≤850µm) were each added to 125 mg P L^{-1} or 1000 mg NH_4^+ L^{-1} solutions
176 respectively, as done in **Section 2.4.1** but 10 mL aliquots of each sample were taken
177 at 2.5, 5, 7.5, 10 and 24 h. Samples were filtered, analysed by Ion Chromatography
178 and the concentration of adsorbed ions were determined.

179 2.4.4 Adsorption isotherms at varying initial concentrations

180 0.1 g of char with highest carbon contents (oak and greenhouse waste) was added
181 to varying concentrations of phosphate solutions, specifically 50-200 mg P L^{-1}, and
182 ammonium concentrations ranging from about 360-815 mg NH_4^+ L^{-1}. These
183 concentrations were chosen to represent some real-case wastewater concentrations.
184 The mixtures were shaken at 160 rpm for 24 h at room temperature, keeping all
185 other parameters identical to batch adsorption tests. Samples were filtered, analysed
186 by Ion Chromatography and the concentration of adsorbed ions were determined as
187 in **Section 2.4.1**.

188

189

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℃ municipal waste biochar and H/C ratios were < 0.7 in all but 4 chars (hydrochars of presscake, greenhouse waste, municipal waste and 400℃ 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%.

213 **3.2 Biochar and hydrochar CEC**

214 CEC is known to decrease with an increase in pyrolysis temperature (Lehmann
215 2007; Silber et al. 2010), but only non-commercial oak chars (OW) exhibited this
216 trend (**Table 2**). Higher temperature biochars (600-650℃) generally had higher CEC
217 than lower temperature biochars (400-450℃). Regardless of their higher oxygen
218 contents, hydrochar CEC values were generally lower than biochar CEC, however,
219 positive correlations between bio- and hydro-char oxygen content and CEC were
220 found ($\rho_{X,Y}$ = 0.8) as expected (Wang et al. 2015b). No relationship between char
221 CEC and surface area was evident; for instance, the CEC of 450℃ commercial oak
222 and 400℃ presscake biochars were similar despite marked differences in surface
223 area (180 m^2 g^{-1} and 2 m^2 g^{-1} respectively). The results indicate that oak and
224 greenhouse waste typically produce a higher CEC than the municipal waste and
225 presscake biochars possibly because these feedstocks contain higher lignocellulosic
226 contents and lower ash contents.

227 To better understand the CEC trends, CEC measurements were performed on chars
228 following solvent extraction in toluene compared with as-received chars. Solvent
229 extraction had different effects on the two types of char: in hydrochars, the CEC in
230 most cases improved (**Fig. 1(a)**); in biochars, the CEC remained unchanged or
231 decreased after solvent extraction, the latter more prevalent for the higher
232 temperature biochars (**Fig. 1(c)**). As CEC is said to be a function of surface area and
233 functionality, an increase in hydrochar CEC following solvent extraction could
234 suggest either the unblocking of pores increasing porosity and surface area, or that a
235 higher surface functionality is being revealed by removing tars. The latter effect may
236 be more important as surface area had negligible influence on char CEC, with
237 hydrochars possessing low surface areas (< 6 m^2 g^{-1}). Based on the assumption that

238 carboxyl and other functional groups improve CEC (Boehm 1994; Glaser et al. 2002;
239 Warner 1977), the removal of volatile hydrocarbons from the surface of the biochar
240 containing these groups by solvent extraction is expected to affect CEC by revealing
241 a different surface functionality below.

242

Table 1. Char physicochemical properties

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

†O content determined by difference.

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245

Table 2. Char pH and mineral composition

Biochar	pH	CEC ($cmol_c$ kg^{-1})	P	K	Ca	Mg	Na
250℃ hydrochars							
Oak wood	4.8	88.3 ± 9.7	1000	0	23,000	0	0
Greenhouse waste	5.8	83.1 ± 19.4	2000	7000	16,000	2000	0
Municipal waste	6.2	44.5 ± 1.7	3000	9000	24,000	4000	0
Presscake from AD	7.2	62.6 ± 3.5	5000	2000	27,000	6000	300
400-450℃ biochars							
Oak wood (commercial)	9.9	59.4 ± 8.1	2000	11,000	44,000	2000	1000
Oak wood	9.7	105.8 ± 12.1	1000	9000	27,000	2000	1000
Greenhouse waste	10.6	109.5 ± 21.8	4000	41,000	36,000	9000	4000
Municpal waste	9.5	65.7 ± 16.2	5000	9000	53,000	5000	8000
Presscake from AD	10.3	51.0 ± 5.5	6000	12000	39,000	6000	4000
600-650℃ biochars							
Oak wood (commercial)	10.3	76.6 ± 0.7	2000	6000	50,000	3000	0
Oak wood	8.6	65.2 ± 20.2	1000	2000	3100	0	0
Greenhouse waste	11.0	146.2 ± 32.3	4000	50,000	45,000	12,000	4000
Municipal waste	10.2	67.9 ± 12.5	5000	9000	81,000	5000	14,000
Presscake from AD	10.1	52.6 ± 11.5	5000	11,000	36,000	5000	4000

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℃ biochars, CEC was slightly higher for the as-received biochars indicating that solvent extraction reduced their surface functionality. There are some anomalies as observed in 400℃ 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).

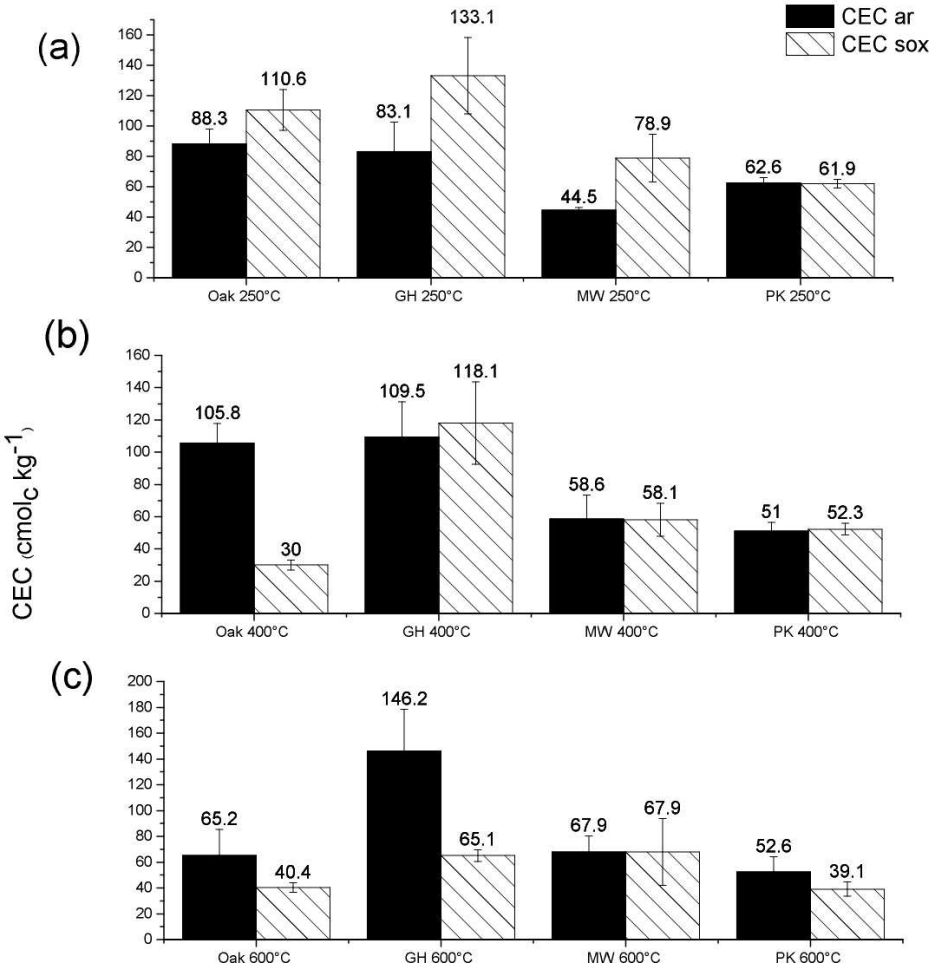

Figure 1. Effect of solvent extraction on biochar CEC
MW: municipal waste; GH: greenhouse waste; PK: presscake
CEC_{ar} and CEC_{sox} refer to CEC before and after solvent extraction respectively

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℃ 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℃ and 650℃ 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℃ and 600℃ 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

290 PO_4-P concentrations. This was also the case for chars in this study, with adsorption
291 efficiencies highest at 170 mg PO_4-P L^{-1} in most cases**.** While pyrolysis temperature
292 and feedstock composition variation did not affect char adsorption capacity
293 substantially, hydrochars generally exhibited lower adsorption capacities.

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

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

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

307 where q_e and q_m = amount of species adsorbed at equilibrium and saturated
308 monolayer adsorption respectively (mg g^{-1}), C_e = equilibrium concentration
309 (mg L^{-1}), n = adsorption intensity, K_a and K_F = Langmuir and Freundlich
310 constants respectively (Ho 2004; Kumar and Sivanesan 2007).

Table 3. Char PO_4-P and NH_4-N sorption capacity

Biochar	PO_4-P				NH_4-N				
	q_e (mg g^{-1})	% PO_4^{3-} ads.	K_d	Desorbed (mg g^{-1})	q_e (mg g^{-1})	% NH_4-N ads.	K_d	Desorbed (mg g^{-1})	Desorbability
250℃ 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℃ 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℃ 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 $C_o \approx 400$ mg L^{-1}; ammonium $C_o \approx 1000$ mg L^{-1}; n.d: not detected; desorbability = ratio of NH_4-N desorbed to NH_4-N adsorbed.

311

312 PO_4-P adsorption was highest a few hours after sorption tests began with the
313 exception of 600℃ greenhouse waste biochar (**Supplemental Fig. A2**). This is
314 contrary to other studies, which observed adsorption equilibrium concentrations after
315 24 h at room temperature (Wang et al. 2011; Zhang et al. 2012). This might be due
316 to the higher PO_4-P concentration used in this study. Oak char kinetics followed a
317 more predictable pattern than greenhouse waste biochars, and based on linear
318 regression analysis, the pseudo-second order model provided the best fit.

319 **3.4 Possible reaction mechanisms for biochar PO_4-P sorption**

320 PO_4-P sorption mechanisms are thought to be dependent on metal ion reactions
321 (precipitation, surface deposition), surface area and surface functionality (Wang et al.
322 2015a; Yao et al. 2013; Zeng et al. 2013). The influence of biochar surface area on
323 PO_4-P adsorption is unclear but some studies suggest that its influence may be
324 minor compared to adsorbent elemental composition. Wang et al. (2015a) for
325 instance found that the best performing biochars did not possess superior surface
326 areas compared to other biochars. Previous studies have also suggested that since
327 biochars tend to be negatively charged, surface functionality may not influence
328 phosphate sorption a great deal (Yao et al. 2011; Zeng et al. 2013).

329 In this study, PO_4-P sorption capacity increased with pyrolysis temperature, with the
330 exception of commercial oak and greenhouse waste biochars (**Fig. 3**). This is in
331 agreement with findings of Wang et al. (2015a) who observed an increase in PO_4-P
332 adsorption with pyrolysis temperature up to a certain point (500℃). Generally, char
333 PO_4-P sorption capacities in this study were found to be lower than other
334 adsorbents, but some positive correlation between PO_4-P adsorption and Ca or Mg
335 contents were observed in hydrochars and biochars, and to a lesser degree with ash
336 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 PO_4-P. Furthermore, Yao et al. (2011) compared biochars produced from raw and from anaerobically digested sugar beet tailings and found that PO_4-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 Ca^{2+}, 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 PO_4-P adsorption capacity was a function of ketones, pyrones and chromens based on a positive correlation of these groups with PO_4-P removal efficiency, although R^2 values of 0.73 suggested that these groups were not solely responsible.

PO_4-P desorption from chars in this study was minimal, hence PO_4-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 PO_4-P desorption might have been because PO_4-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 desorbabilty increased to some extent with an increase in amount of adsorbed phosphate.

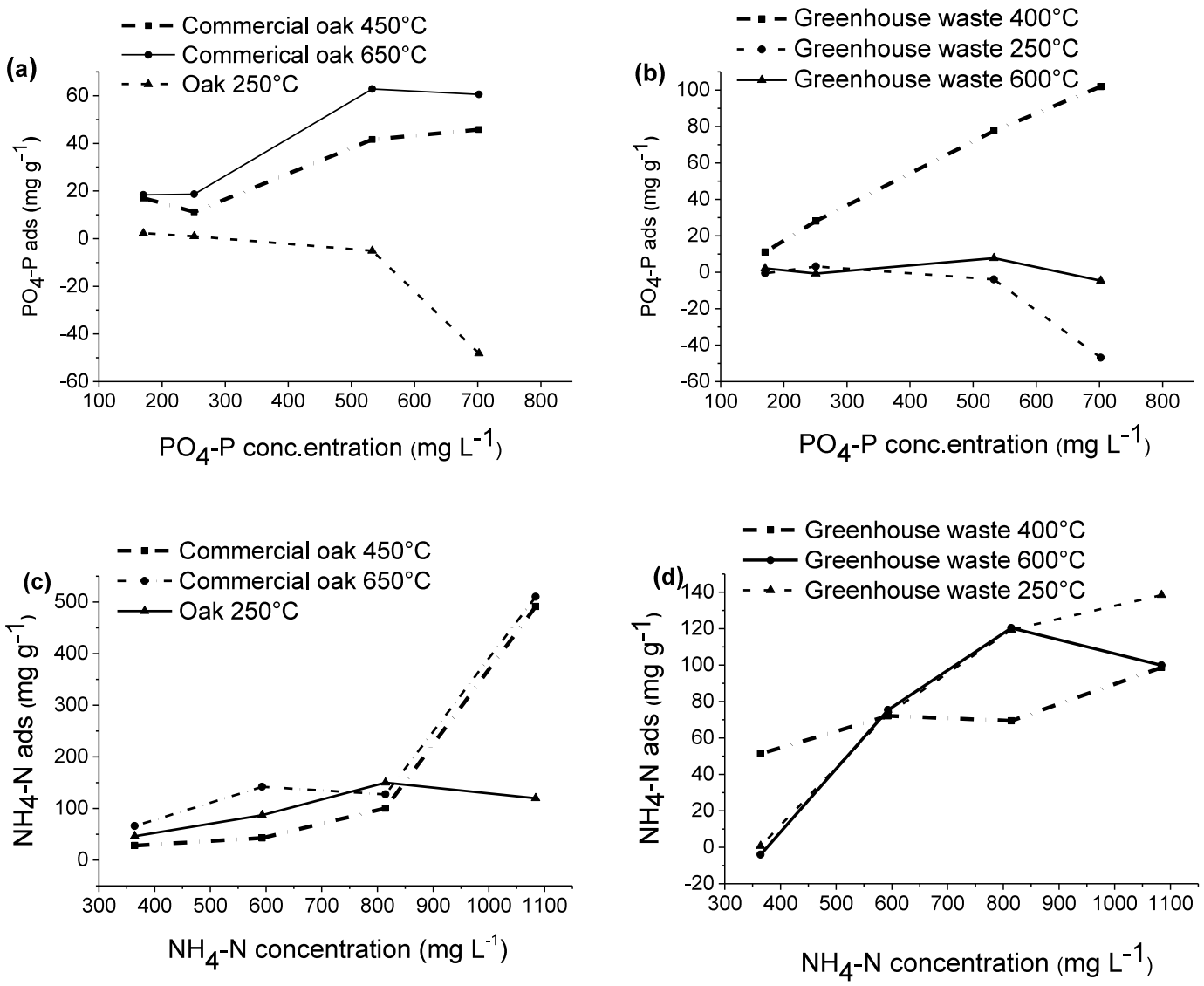

Figure 2. Effect of increasing PO_4-P and NH_4-N concentration on sorption on oak and greenhouse waste chars

361 Data fitted to kinetic models showed that the pseudo-second order model
362 consistently gave a closer fit compared to the pseudo-first order and intra-particle
363 diffusion models. While the latter two models gave average R^2 values of 0.53 and
364 0.28 respectively, the pseudo-second order R^2 values were higher (**Supplemental**
365 **Table A1)**. Previous studies have also observed many metals and heavy elements
366 follow this pattern (Limousin et al. 2007). Wang et al. (2011) also found this model
367 fitted better than the intra-particle diffusion model. Based on their adsorption kinetics
368 data, simultaneous rapid surface adsorption of PO_4-P and slower intra-particle
369 diffusion through the adsorbent occurred simultaneously.

370 Solvent extraction had variable effects on char PO_4-P adsorption (**Fig. 3**). PO_4-P
371 adsorption improved in some low temperature biochars (400-450℃); 400℃ oak
372 biochar which released phosphate into solution prior to extraction performed
373 marginally better after extraction. For 600-650℃ biochars, solvent extraction
374 decreased % PO_4^{-}P adsorption however. These did not appear to be related to
375 volatile matter, ash content or elemental composition.

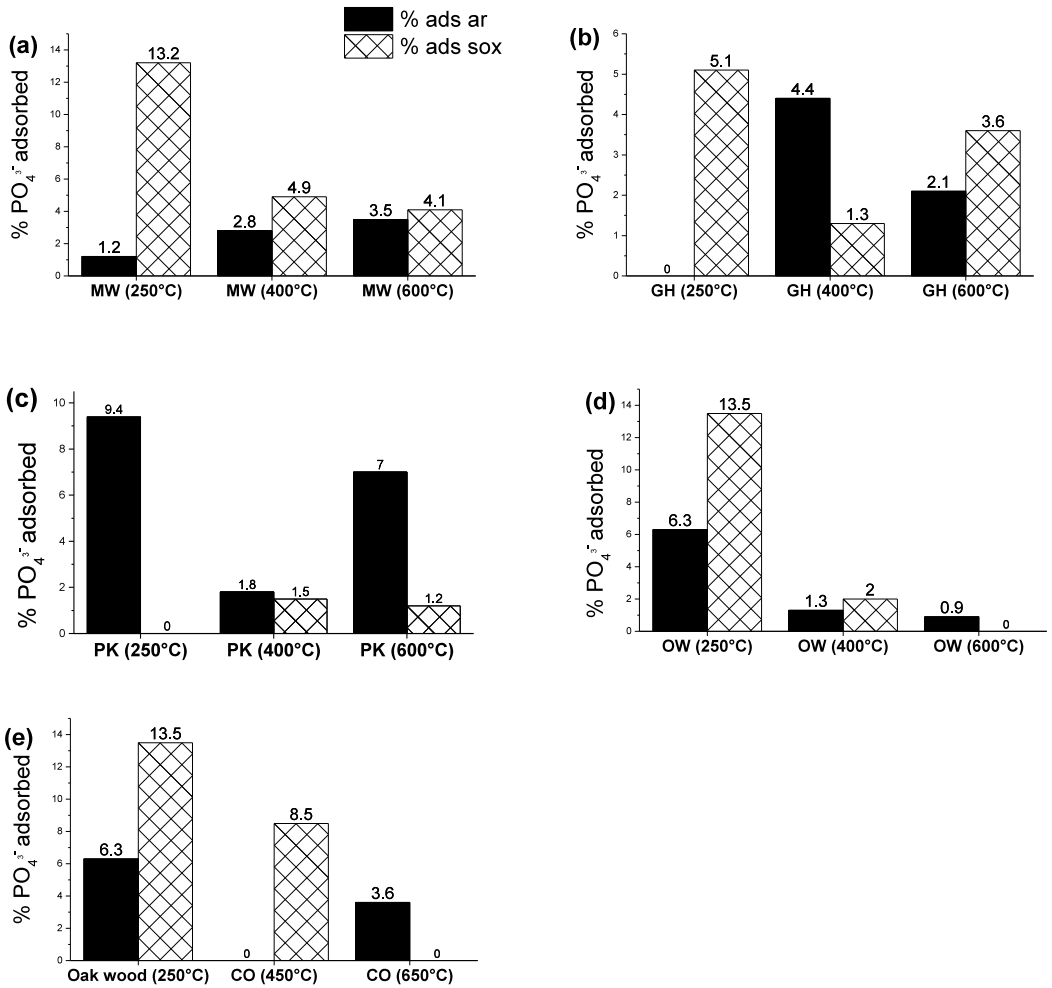

Figure 3. Comparison of PO_4-P adsorption capacities of solvent extracted and non-extracted chars

PK: presscake; MW: municipal waste; CO: commercial oak; GH: greenhouse waste; OW: oak wood biochars solvent extracted chars are denoted 'sox'

385 **3.5 Char NH_4-N sorption**

386 Previous studies have shown that pH, time and initial NH_4^+ concentrations are
387 important factors that determine biochar adsorption capacity (Fernando et al. 2005;
388 Kizito et al. 2015; Schlegel et al. 1999). NH_4-N adsorption increased at higher initial
389 solution concentrations but only to a certain point for oak hydrochar and 600℃
390 greenhouse waste biochar (**Figs. 2(c)-(d)**). Preliminary results showed that many
391 biochars released, rather than adsorbed NH_4-N at initial concentrations below 400
392 mg L^{-1} (data not included). However, this may not be resulting from the lower initial
393 concentration since biochars are capable of adsorbing NH_4-N at low concentrations.
394 Subsequent adsorption tests with untreated biochars were however performed at a
395 higher initial concentration of about 1000 mg NH_4^+ L^{-1} and presented in **Table 3**.
396 NH_4-N adsorption data were fitted to the linearized Langmuir and Freundlich
397 isotherm models, and although not an optimal fit, the Langmuir isotherm model
398 described ammonium adsorption better, based on higher R^2 values (0.75-0.91 for
399 commercial oak chars and 0.91 for greenhouse waste 250℃ and 600℃). As
400 observed in char PO_4-P sorption, the pseudo-second order model generally had
401 higher R^2 values (**Table 5**) compared to the pseudo-first order and intra-particle
402 diffusion models, although not an optimal fit in many cases.

403 Desorption of NH_4-N after KCl extraction was minimal and this has been observed
404 elsewhere (Clough et al. 2013; Fernando et al. 2005; Saleh et al. 2012). This might
405 have been because NH_4-N was effectively trapped within the biochar pore structure,
406 because the salt solution (KCl) was not effective in extracting adsorbed NH_4-N
407 (Saleh et al. 2012), or due to NH_3-N volatilization especially for high pH biochars
408 (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℃) 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

434 adsorption in complex solutions (dairy or swine effluents) compared to simple
435 solutions (ammonium chloride) (Fernando et al. 2005; Sarkhot et al. 2013), although
436 the reverse effect has also been observed, as in Kizito et al. (2015). No clear trends
437 were observed between char organic matter content and NH_4-N adsorption capacity
438 in this study.

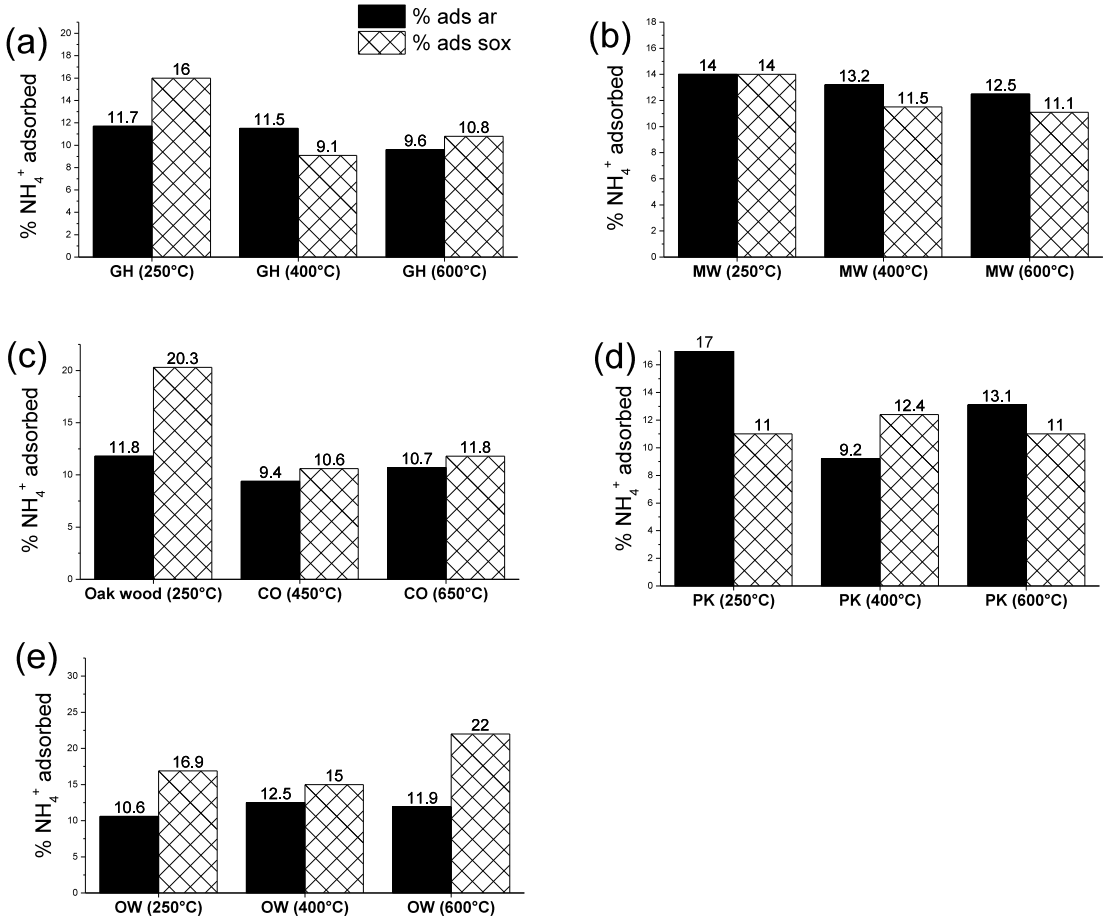

Figure 4. Comparison of NH_4-N adsorption capacities of solvent extracted and non-extracted chars showing variable trends; solvent extracted chars denoted by prefix 'S'.

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

440 **Conclusions**

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

447 Char PO_4-P and NH_4-N sorption capacities ranged from about 0-30 mg g^{-1} and
448 105.8-146.4 mg g^{-1} respectively with generally low desorption of both ions. Biochar
449 phosphate adsorption capacity increased with pyrolysis temperature, possibly due to
450 metal ion precipitation reactions between phosphate and char calcium and
451 magnesium. In contrast, a positive relationship between char oxygen functional
452 groups, CEC and NH_4-N adsorption suggested that NH_4-N adsorption may have
453 occurred mainly via chemical reactions with oxygen-containing functional groups
454 rather than ion-exchange/physisorption. Overall however, in spite of differences in
455 physicochemical properties and processing conditions, there was no great variation
456 in char phosphate and ammonium sorption capacities between the chars.

457

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References

Bargmann, I., Rillig, M.C., Kruse, A., Greef, J.M., Kücke, M., 2014. Effects of hydrochar application on the dynamics of soluble nitrogen in soils and on plant availability. J. Plant Nutr. Soil Sci. 177, 48–58. doi:10.1002/jpln.201300069

Barker, J., Zublena, J., Wallis F., 2001. Animal and Poultry Manure Production and Characterization, North Carolina State University Cooperative Extension. https://www.bae.ncsu.edu/topic/animal-waste-mgmt/program/land-ap/barker/a&pmp&c/content.htm

Battistoni, P., Carniani, E., Fratesi, V., Balboni, P., Tornabuoni, P., 2006. Chemical−Physical Pretreatment of Phosphogypsum Leachate. Ind. Eng. Chem. Res. 45, 3237–3242. doi:10.1021/ie051252h

Biederman, L.A., Harpole, W.S., 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. GCB Bioenergy 5, 202–214. doi:10.1111/gcbb.12037

Boehm, H.P., 1994. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon N. Y. 32, 759–769. doi:10.1016/0008-6223(94)90031-0

Borchard, N., Wolf, A., Laabs, V., Aeckersberg, R., Scherer, H., Moellerand, A., Amelung, W., 2012. Physical activation of biochar and its meaning for soil fertility and nutrient leaching- A greenhouse experiment, Soil Use Manage. 28:177-184. doi: 10.1111/j.14752743.2012.00407.x

Bott, C.B., Brummer, J., Koon, J., 2003. Physical-chemical pretreatment of process wastewater from a phsophorus plant for discharge to a POTW. In: Bowers, A., and W. Eckenfelder. 2003. Industrial wastewater and Best Available Treatment technologies: Performance, reliability, and economics, DEStech Publications Inc.

Brewer, C.E., 2012. Biochar Characterisation and Engineering. http://lib.dr.iastate.edu/etd/12284/

Cai, T., Park, S.Y., Li, Y., 2013. Nutrient recovery from wastewater streams by microalgae: Status and prospects. Renew. Sustain. Energy Rev. 19, 360–369. doi:10.1016/j.rser.2012.11.030

Chen, B., Chen, Z., Lv, S., 2011. A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. Bioresour. Technol. 102, 716–23. doi:10.1016/j.biortech.2010.08.067

Clough, T., Condron, L., Kammann, C., Müller, C., 2013. A Review of Biochar and Soil Nitrogen Dynamics. Agronomy 3, 275–293. doi:10.3390/agronomy3020275

Collison, M., Collison, L., Sakrabani, R., Tofield, B., Wallage, Z., 2009. Biochar and Carbon Sequestration: A Regional Perspective: A Report Prepared for East of England Development Agency (EEDA). https://www.uea.ac.uk/polopoly_fs/1.118134!LCIC%20EEDA%20BIOCHAR%20REVIEW%202004-09.pdf

Fernando, W.A., Xia, K., Rice, C.W., 2005. Sorption and Desorption of Ammonium from Liquid Swine Waste in Soils. Soil Sci. Soc. Am. J. 69, 1057. doi:10.2136/sssaj2004.0268

Gaskin, J., Steiner, C., Harris, K., Das, K., Bibens, B., 2008. Effect of low-temperature pyrolysis conditions on biochar for agricultural use, T. Am. Soc. Agr. Biol. Eng. 51, 2061-2069.

Glaser, B., Lehmann, J., Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - a review. Biol. Fertil. Soils 35, 219–230. doi:10.1007/s00374-002-0466-4

Grzmil, B., Wronkowski, J., 2006. Removal of phosphates and fluorides from industrial wastewater. Desalination 189, 261–268. doi:10.1016/j.desal.2005.07.008

Heilmann, S.M., Jader, L.R., Harned, L.A., Sadowsky, M.J., Schendel, F.J., Lefebvre, P.A., von Keitz, M.G., Valentas, K.J., 2011. Hydrothermal carbonization of microalgae II. Fatty acid, char, and algal nutrient products. Appl. Energy 88, 3286–3290. doi:10.1016/j.apenergy.2010.12.041

Ho, Y., 2004. Selection of optimum sorption isotherm. Carbon. 42, 2113-2130. doi:10.1016/j.carbon.2004.03.019

International Biochar Initiative, 2014. Standardized product definition and product testing guidelines for biochar that is used in soil. http://www.biochar-international.org/sites/default/files/IBI_Biochar_Standards_V2%200_final_2014.pdf

Kastner,J.R., Miller, J., Das, K., 2009. Pyrolysis conditions and ozone oxidation effects on ammonia adsorption in biomass generated chars. J. Haz. Mat. 164, 1420-1427. doi:10.1016/j.jhazmat.2008.09.051

Kizito, S., Wu, S., Kirui, W., Lei, M., Lu, Q., Bah, H., Dong, R., 2015. Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry, Sci.Total Environ. 505, 102-112. doi:10.1016/j.scitotenv.2014.09.096

Krishnan, K.A., Haridas, A., 2008. Removal of phosphate from aqueous solutions and sewage using natural and surface modified coir pith. J. Hazard. Mater. 152, 527–35. doi:10.1016/j.jhazmat.2007.07.015

Kumar, K.V., Sivanesan, S., 2007. Sorption isotherms for safranin onto rice husk: Comparison of linear and non-linear methods. Dyes Pigments. 72, 130-133. doi:10.1016/j.dyepig.2005.07.020

Laird, D., Fleming, P., Wang, B., Horton, R., Karlen, D., 2010a. Biochar impact on nutrient leaching from a Midwestern agricultural soil. Geoderma 158, 436–442. doi:10.1016/j.geoderma.2010.05.012

Laird, D.A., Fleming, P., Davis, D.D., Horton, R., Wang, B., Karlen, D.L., 2010b. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. Geoderma 158, 443–449. doi:10.1016/j.geoderma.2010.05.013

Lehmann, J., 2007. Bio-energy in the black. Front. Ecol. Environ. 5, 381–387. doi:10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizão, F.J., Petersen, J., Neves, E.G., 2006. Black Carbon Increases Cation Exchange Capacity in Soils. Soil Sci. Soc. Am. J. 70, 1719. doi:10.2136/sssaj2005.0383

Limousin, G., Gaudet, J.-P., Charlet, L., Szenknect, S., Barthès, V., Krimissa, M., 2007. Sorption isotherms: A review on physical bases, modeling and measurement. Appl. Geochemistry 22, 249–275. doi:10.1016/j.apgeochem.2006.09.010

Liu, J.C., 2009. Recovery of phosphate and ammonium as struvite from semiconductor wastewater. Sep. Purif. Technol. 64, 368–373. doi:10.1016/j.seppur.2008.10.040

Mukherjee, A., Zimmerman, A.R., 2013. Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar–soil mixtures. Geoderma 193-194, 122–130. doi:10.1016/j.geoderma.2012.10.002

Poerschmann, J., Weiner, B., Koehler, R., Kopinke, F.-D., 2015. Organic breakdown products resulting from hydrothermal carbonization of brewer's spent grain. Chemosphere 131, 71–7. doi:10.1016/j.chemosphere.2015.02.057

Rittmann, B.E., Mayer, B., Westerhoff, P., Edwards, M., 2011. Capturing the lost phosphorus. Chemosphere 84, 846–853. doi:10.1016/j.chemosphere.2011.02.001

Saleh, M.E., Mahmoud, A., Rashad, M., 2012. Peanut biochar as a stable adsorbent for removing NH_4-N from wastewater: A preliminary study, Adv. Environ. Biol. 6, 2170-2176. doi:10.3390/agronomy3020275

Sakadevan, K., Bavor, H.J., 1998. Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems. Water Res. 32, 393–399. doi:10.1016/S0043-1354(97)00271-6

Sarkhot, D. V, Berhe, A.A., Ghezzehei, T.A.,. Impact of biochar enriched with dairy manure effluent on carbon and nitrogen dynamics. J. Environ. Qual. 41, 1107–14. doi:10.2134/jeq2011.0123

Silber, A., Levkovitch, I., Graber, E.R., 2010. pH-dependent mineral release and surface properties of cornstraw biochar: agronomic implications. Environ. Sci. Technol. 44, 9318–23. doi:10.1021/es101283d

Song, Y.-H., Qiu, G.-L., Yuan, P., Cui, X.-Y., Peng, J.-F., Zeng, P., Duan, L., Xiang, L.-C., Qian, F., 2011. Nutrients removal and recovery from anaerobically digested swine wastewater by struvite crystallization without chemical additions. J. Hazard. Mater. 190, 140–9. doi:10.1016/j.jhazmat.2011.03.015

Spokas, K.A., Novak, J.M., Venterea, R.T., 2011. Biochar's role as an alternative N-fertilizer: ammonia capture. Plant Soil 350, 35–42. doi:10.1007/s11104-011-0930-8

USEPA, 2002. Onsite wastewater treatment systems manual. http://water.epa.gov/aboutow/owm/upload/2004_07_07_septics_septic_2002_osdm_all.pdf

Uzoma, K.C., Inoue, M., Andry, H., Fujimaki, H., Zahoor, A., Nishihara, E., 2011. Effect of cow manure biochar on maize productivity under sandy soil condition. Soil Use Manag. 27, 205–212. doi:10.1111/j.1475-2743.2011.00340.x

Vasanth Kumar, K., Sivanesan, S., 2007. Sorption isotherm for safranin onto rice husk: Comparison of linear and non-linear methods. Dye. Pigment. 72, 130–133. doi:10.1016/j.dyepig.2005.07.020

Wang, Z., Nie, E., Li, J., Yang, M., Zhao, Y., Luo, X., Zheng, Z., 2011. Equilibrium and kinetics of adsorption of phosphate onto iron-doped activated carbon. Environ. Sci. Pollut. Res. Int. 19, 2908–17. doi:10.1007/s11356-012-0799-y

Wang, Z., Guo, H., Shen, F., Yang, G., Zhang, Y., Zeng, Y., Wang, L., Xiao, H., Deng, S., 2015a. Biochar produced from oak sawdust by Lanthanum (La)-involved pyrolysis for adsorption of ammonium (NH_4^+), nitrate (NO_3^-), and phosphate (PO_4^{3-}). Chemosphere 119, 646–653. doi:10.1016/j.chemosphere.2014.07.084

Wang, B., Lehmann, J., Hanley, K., Hestrin, R., Enders, A., 2015b. Adsorption and desorption of ammonium by maple wood biochar as a function of oxidation and pH. Chemosphere 138, 120–126. doi:10.1016/j.chemosphere.2015.05.062

Warner, S.A., 1977. Cation exchange properties of forest litter as influenced by vegetation type and Decomposition. http://andrewsforest.oregonstate.edu/pubs/pdf/pub533.pdf

Xu, G., Sun, J., Shao, H., Chang, S.X., 2014. Biochar had effects on phosphorus sorption and desorption in three soils with differing acidity. Ecol. Eng. 62, 54–60. doi:10.1016/j.ecoleng.2013.10.027

Xue, Y., Hou, H., Zhu, S., 2009. Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag. J. Hazard. Mater. 162, 973–80. doi:10.1016/j.jhazmat.2008.05.131

Xue, Y., Gao, B., Yao, Y., Inyang, M., Zhang, M., Zimmerman, A.R., Ro, K.S., 2012. Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests. Chem. Eng. J. 200-202, 673–680. doi:10.1016/j.cej.2012.06.116

Yamato, M., Okimori, Y., Wibowo, I.F., Anshori, S., Ogawa, M., 2006. Effects of the application of charred bark of Acacia mangium on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. Soil Sci. Plant Nutr. 52, 489–495. doi:10.1111/j.1747-0765.2006.00065.x

Yao, Y., Gao, B., Chen, J., Yang, L., 2013. Engineered biochar reclaiming phosphate from aqueous solutions: mechanisms and potential application as a slow-release fertilizer. Environ. Sci. Technol. 47, 8700–8. doi:10.1021/es4012977

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L., 2011. Biochar derived from anaerobically digested sugar beet tailings: characterization and phosphate removal potential. Bioresour. Technol. 102, 6273–8. doi:10.1016/j.biortech.2011.03.006

Ye, Y., Hou, H., Zhu, S., 2006. Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag, J. Hazard. Mater.162, 973-980. doi: 10.1016/j.jhazmat.2008.05.131

Ye, Z.L., Chen, S.H., Wang, S.M., Lin, L.F., Yan, Y.J., Zhang, Z.J., Chen, J.S., 2010. Phosphorus recovery from synthetic swine wastewater by chemical precipitation using response surface methodology. J. Hazard. Mater. 176, 1083–8. doi:10.1016/j.jhazmat.2009.10.129

Yuan, J.-H., Xu, R.-K., Zhang, H., 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresour. Technol. 102, 3488–97. doi:10.1016/j.biortech.2010.11.018

Zeng, Z., Zhang, S., Li, T., Zhao, F., He, Z., Zhao, H., Yang, X., Wang, H., Zhao, J., Rafiq, M.T., 2013. Sorption of ammonium and phosphate from aqueous solution by biochar derived from phytoremediation plants. J. Zhejiang Univ. Sci. B 14, 1152–61. doi:10.1631/jzus.B1300102

Zhang, M., Gao, B., Yao, Y., Xue, Y., Inyang, M., 2012. Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions. Chem. Eng. J. 210, 26–32. doi:10.1016/j.cej.2012.08.052

Zhao, L., Cao, X., Mašek, O., Zimmerman, A., 2013. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. J. Hazard. Mater. 256-257, 1–9. doi:10.1016/j.jhazmat.2013.04.015

Zheng, W., Sharma, B.K., Rajagopalan, N., 2010. Using Biochar as a Soil Amendment for Sustainable Agriculture. https://www.ideals.illinois.edu/handle/2142/25503