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Adsorption and desorption of ammonium by maple wood biochar as a function of oxidation and pH

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HIGHLIGHTS

- Oxidizing biochars at their lowered pH did not increase ammonium adsorption.
- Adsorption was not fully reversible in aqueous solution.
- Extraction with KCl extracts nearly all adsorbed ammonium.
- Unrecovered ammonium was negligible at high oxidation, but increased at high pH.
- Unrecovered ammonium has likely been volatilized as ammonia.

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ABSTRACT

The objective of this work was to investigate the retention mechanisms of ammonium in aqueous solution by using progressively oxidized maple wood biochar at different pH values. Hydrogen peroxide was used to oxidize the biochar to pH values ranging from 8.1 to 3.7, with one set being adjusted to a pH of 7 afterwards. Oxidizing the biochars at their lowered pH did not increase their ability to adsorb ammonium. However, neutralizing the oxygen-containing surface functional groups on oxidized biochar to pH 7 increased ammonia adsorption two to three-fold for biochars originally at pH 3.7–6, but did not change adsorption of biochars oxidized to pH 7 and above. The adsorption characteristics of ammonium are well described by the Freundlich equation. Adsorption was not fully reversible in water, and less than 27% ammonium was desorbed in water in two consecutive steps than previously adsorbed, for biochars with a pH below 7, irrespective of oxidation. Recovery using an extraction with 2 M KCl increased from 34% to 99% of ammonium undesorbed by both preceding water extractions with increasing oxidation, largely irrespective of pH adjustment. Unrecovered ammonium in all extractions and residual biochar was negligible at high oxidation, but increased to 39% of initially adsorbed amounts at high pH, likely due to low amounts adsorbed and possible ammonia volatilization losses.

1. Introduction

A significant portion of fertilizer N is lost from agricultural fields by leaching (Raun and Johnson, 1999). Such a loss is not only of economic concern for the farmer, but also bears an environmental consequence of pollution of ground and surface waters including marine ecosystems (Carpenter et al., 1998). In addition to improved timing and dosing of N applications, also an improved retention of N in the soil will help in enhancing the use efficiency of applied fertilizers (Vitousek et al., 1997; Steiner et al., 2008).

Biochar applications to soil have in several cases been shown to increase N retention (Steiner et al., 2008), to improve N use efficiency (Zwieten et al., 2010), and to reduce leaching losses of N (Güereña et al., 2013). Biochar is a carbonaceous organic matter generated by heating under oxygen-limited conditions, comparable to charcoal (Laird, 2008; Lehmann and Joseph, 2009). Similar to other organic matter in soil, biochar generally does not contain appreciable amounts of anion exchange capacity (Cheng et al., 2008) and therefore does not retain nitrate (Hollister et al., 2012). Only reductions in ammonium leaching may at least partly be attributed to adsorption to biochar (Lehmann et al., 2003), even

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though reductions in nitrate leaching have been observed and explained with retention by microbial N cycling (Güereña et al., 2013).

Ammonium retention by biochar may be readily explained by electrostatic adsorption to negatively charged oxygen-containing surface functional groups (Cheng et al., 2006; Hale et al., 2013). Freshly produced biochars typically have very low ability to adsorb ammonium (Yao et al., 2012). Over time, biochar surfaces are oxidized and cation retention increases (Cheng et al., 2008, 2014), to levels greater than other organic matter in soils (Liang et al., 2006). Oxidation may also be done intentionally as part of an effort to improve nutrient retention by biochars.

The typically rather small domains of fused aromatic rings of many biochars (Nguyen et al., 2010) are densely decorated with oxidized functional groups when exposed to soil for long periods of time (Mao et al., 2012). In soil, the effect of this surface oxidation on ammonium adsorption cannot be clearly distinguished from the effect of adsorbed organic matter on cation exchange capacity, even though oxidation is perceived to be more important (Liang et al., 2013). Ammonium adsorbed by negatively charged organic functional groups on biochar surfaces should be fully desorbable by KCl (Clough et al., 2013). However, results of desorption from peanut biochar showed low desorbability with KCl (Saleh et al., 2012). It is not clear whether oxidation of biochar surfaces would change this low desorbability, which would implicate other processes in addition to electrostatic adsorption in the retention mechanism.

The objectives of this study were to (i) quantify the relationship between oxidation and ammonium retention; and (ii) investigate whether ammonium adsorption to oxidized surfaces is fully reversible. We hypothesized that (i) oxidation increases the affinity of ammonium to biochar and decreases desorption in water; and (ii) ammonium adsorption is not fully reversible using KCl irrespective of oxidation.

2. Experimental methods and materials

2.1. Preparation of biochar

Maple wood biochars (20% sugar maple, 80% red maple) which were pyrolysed at 500 °C using a modified muffle furnace (Thermo Scientific, Waltham, MA, USA) under argon atmosphere (sweep of 1 L min^{-1}), were ground and sieved to between 149 and 850 μm to obtain a uniform particle size. The residence time in the reactor was 30 min and the heating rate was 2.5 °C min^{-1}. The muffle furnace is equipped with a cooling system using copper coils with circulating water. The original biochar had 78.9% fixed carbon, 19.7% volatile matter and 1.4% ash content (wt.% dry), respectively (ASTM, 2007). Before use, all empty glassware and PE centrifuge tubes were acid washed in a hydrochloric acid bath (10% HCl) and rinsed with deionized water (DIW) to minimize contamination. The biochars were oxidized by using different concentrations of H_2O_2 as well as different exposure times at 30 °C, in comparison to DIW for 100 h, all using a solid-to-liquid ratio of 1:10 (w/v) (Table 1). Earlier experiments showed that exposure to water mildly oxidizes biochars abiotically (Cheng et al., 2006). H_2O_2 was chosen in order to minimize precipitation, complexation or analytical interferences which have been observed with other oxidants (e.g., H_2SO_4, HNO_3) (Chen and Wu, 2004). After oxidation, the H_2O_2 was removed by filtration under suction using a Büchner funnel, fitted with a Whatman No. 1 filter paper, and the oxidized biochars were rinsed with DIW. The pH values of biochars were determined using a glass electrode (detection limit of 0.01 pH units) with a biochar-to-water ratio of 1:20 (w/v) (Orion 3-Star pH Benchtop; Thermo Electron Corporation, Beverly, MA, USA) (Cheng and Lehmann, 2009). After determining the initial pH values of the oxidized biochar samples, the biochars were dried at 60 °C for 48 h, and then separated into two identical batches. One batch was utilized as it remained after oxidation and drying; for the other, hydrochloric acid (1.0 M) or sodium hydroxide solution (1.0 M) was used to adjust the pH values to 7.00 ± 0.01, respectively. The reason for doing so was that cation exchange capacity is known to significantly change with different pH of biochars (Cheng et al., 2008) and presumably also ammonium adsorption behavior; since oxidation resulted in different pH values, adjusting the pH to a uniform pH of 7 allowed comparison of adsorption as a result of oxidation without the effect of differential pH. The pH values were adjusted every 24 h until they reached equilibrium, then suspensions were filtered through Whatman No. 1 filter paper, and dried similar to unadjusted biochars.

The specific surface area (SSA) and pore size distribution of the biochars were evaluated using the ASAP 2020 – Physisorption Analyzer (BET) CO_2 adsorption technique at 273.15 K. Elemental C, H, O, N and S of biochars were determined on a Temperature Conversion Elemental Analyzer (TC/EA). Proximate analysis was conducted using ASTM D1762-84 Chemical Analysis of Wood Charcoal after modification to accommodate biochar reactivity (Enders et al., 2012). Total elemental contents of biochars were conducted using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Enders and Lehmann, 2012).

2.2. Adsorption experiments

Batch adsorption experiments were conducted in PE centrifuge tubes at room temperature. All adsorption experiments were performed in triplicate. In order to test whether the desorption was

Table 1
Biochar exposure to oxidant (at 33–35 °C) and their physical and chemical properties (means and standard errors; $n = 3$; additional biochar properties in Supplementary Online Tables S1 and S2).

Solute	Concentration (%)	Oxidization time (h)	pH	Elemental contents							Surface area
				C_{tot}[a] (w%)	H (wt.%)	O (wt.%)	N (wt.%)	S (wt.%)	H/C_{tot} (mol mol^{-1})	O/C_{tot} (mol mol^{-1})	BET-CO_2 ($m^2 g^{-1}$)
None	n/a	n/a	8.70	88.2	3.09	11.4	0.18	0.03	0.42	0.10	257
H_2O	n/a	100	8.13	86.0	2.78	10.7	0.18	0.07	0.39	0.09	254
H_2O_2	15	0.75	7.53	83.9	2.81	12.0	0.17	0.06	0.40	0.11	251
H_2O_2	30	0.25	7.44	82.1	2.71	11.2	0.18	0.01	0.40	0.10	251
H_2O_2	30	6	5.97	82.1	2.21	11.1	0.19	0.04	0.32	0.10	251
H_2O_2	30	110	4.37	78.0	2.70	17.6	0.15	0.02	0.42	0.17	226
H_2O_2	30	350	3.69	73.6	2.57	21.4	0.15	0.04	0.42	0.22	225
P-value[b]	n/a	n/a	0.106	0.061	0.814	0.012	0.101	0.470	0.500	0.008	0.082

[a] C_{tot} is the total carbon of biochar.

[b] P-value for a linear regression of the effect of duration of H_2O_2 exposure (only including no H_2O_2 and 30%).

complete or not and whether we lost ammonium during the experiment, we used ^{15}N labelling to observe whether the ammonium N we did not recover was still in the biochar. 0.5 g of the dried biochar was added into 50-mL centrifuge tubes containing 40 mL of solution with 0, 5, 10, 50, or 100 mg NH_4-N L^{-1} (containing 10% of ^{15}N-enriched ammonium sulfate (10 atom% ^{15}N excess; Cambridge Isotope Lab, Inc.)). The tubes were shaken at 400 rpm in a mechanical shaker for 16 h and then centrifuged at 2500 rpm for 10 min, and the supernatant was carefully aspirated using a Pasteur pipette. Ammonium N concentration in the supernatant (fully mixed and equilibrated with the solution remaining in the biochar during shaking) was determined immediately using a continuous flow analyzer (Bran and Luebbe Autoanalyzer, SPX, Charlotte, NC).

2.3. Desorption experiments

After the adsorption, the solution remaining in the tubes was decanted and 40 mL of ultrapure water (>18.2 MΩ cm) which was prepared by a Barnstead E-pure water purifier was added as described for the adsorption experiment described above. This procedure was repeated twice, generating two desorption steps. Ammonium N concentrations in the supernatant were determined within 24 h by using the continuous flow analyzer.

After the desorption with ultrapure water, all the liquids in the tubes were decanted and 40 mL 2 M KCl were added into the centrifuge tubes to extract the absorbed ammonium from the biochar. This procedure was repeated once as mentioned above for the desorption only using initial concentrations of 5, 10, and 50 mg NH_4-N L^{-1}. Ammonium nitrogen concentrations were determined immediately by using the continuous flow analyzer.

The remaining biochar after KCl extraction (only using experiments with an initial concentration of 50 mg NH_4-N L^{-1}) was rinsed with DIW and dried at 60 °C for 48 h. A sub-sample of the dried biochar was finely ground for analysis of total ^{15}N by a Thermo Delta V Isotope Ratio Mass Spectrometry.

2.4. Data analyses

The results of adsorption and desorption experiments were the average of three replications. Adsorption data were fitted to both Freundlich and Langmuir isotherm models using the following equations:

$$\text{Langmuir isotherm}: \quad q_e = Q_o \cdot k_L \cdot C_e/(1 + k_L \cdot C_e) \qquad (1)$$

$$\text{Freundlich isotherm}: \quad q_e = k_f \cdot C_e^{1/n} \qquad (2)$$

where q_e (mg NH_4^+-N L^{-1}) is the adsorption capacity; C_e (mg NH_4^+-N L^{-1}) is the equilibrium concentration after the adsorption or desorption; $1/n$ (dimensionless) is the intensity of adsorption or affinity; k_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) is the Freundlich adsorption constant; Q_o (mg NH_4^+-N g^{-1}) is the maximum sorption capacity; k_L (L mg^{-1}) is a Langmuir constant. The data were fitted to these equations using non-linear regression and the goodness of fits, the sum of squares (R_{sqr}) associated with the model results were calculated using SigmaPlot 12.5 (SAS, Cary, NC). Charge was calculated from the maximum sorption capacity Q_o (mg NH_4-N g^{-1}) through dividing the Q_o by the molar mass of ammonium and multiplying by its charge of 1.

3. Results

3.1. Characteristics of oxidized biochars

With increasing oxidization time, the pH of the tested biochar gradually decreased from an initial value of 8.70–3.69 (Table 1). The oxidation of the biochar with H_2O_2 resulted in a doubling of the O content, a 16% decrease in the H content and a 20% decrease in the C content (Table 1). The SSA decreased by only 12% with oxidation.

3.2. Adsorption and desorption

With increasing oxidation and a consequent lowering of pH, the adsorption capacity remained unchanged (Fig. 1a). However, if the pH of the biochar was adjusted to 7 after oxidation, the adsorption capacity of the most strongly oxidized biochar increased more than four-fold (Fig. 1b). The maximum adsorption capacity Q_o reached 5 mg NH_4-N L^{-1} for the longest oxidation period, in comparison to less than 1 mg NH_4-N L^{-1} for the weakly oxidized or unoxidized biochars (Table 2; using the Langmuir isotherm; both approaches gave good fits). This translated into a maximum surface charge of 302 mmolc kg^{-1} with the highest oxidation and pH adjustment (Fig. 2).

Desorption experiments with water hardly decreased the amount of ammonium adsorbed (Fig. 3). For the highest oxidation, as an example, this is illustrated by an essentially flat arrow from the adsorption to second desorption. For an initial concentration of 50 mg L^{-1}, the decrease amounted on average to less than 27% of initially adsorbed ammonium. In contrast, the equilibrium

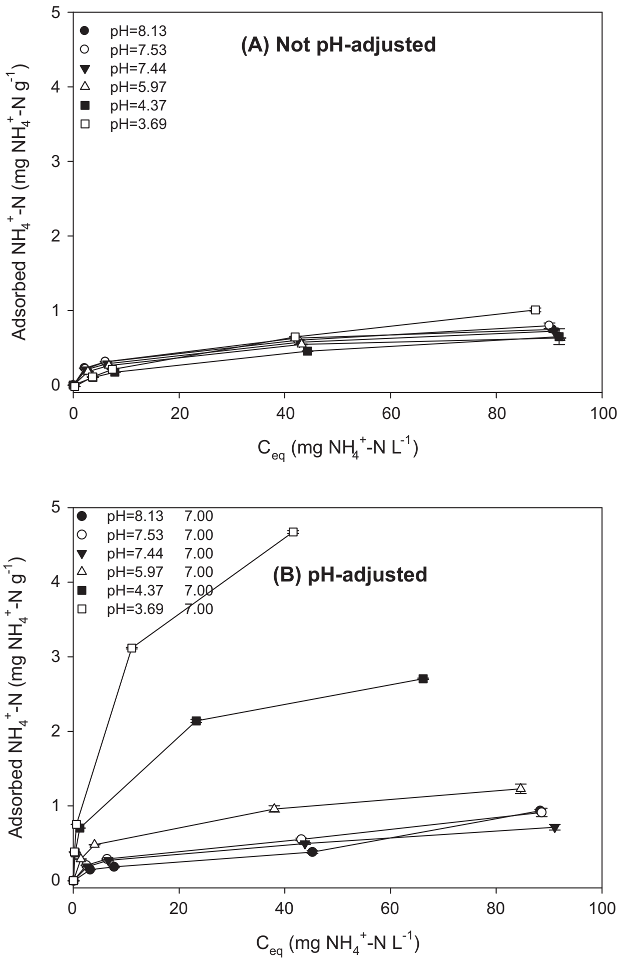

Fig. 1. Adsorption isotherms of ammonium at pH values (Not pH-adjusted and pH-adjusted) after oxidation. Error bars represent standard error of triplicate samples ($n = 3$). Symbols may cover error bars. C_{eq} is the equilibrium concentration of ammonium in aqueous solution (mg NH_4^+-N L^{-1}).

Table 2
Parameter results for the fit of the Freundlich and Langmuir isotherms to the adsorption experimental data of oxidized biochars and oxidized biochars for which the pH has been adjusted to 7 (indicated by an arrow) (for variability see Fig. 1, standard error is less than 6% of the mean throughout).

pH of oxidized biochar	Langmuir adsorption model			Freundlich adsorption model		
	Q_o (mg NH_4^+-N g^{-1})	k_L	R_{sqr}	k_f	$1/n$	R_{sqr}
pH = 3.69	1.77	0.01	0.995	0.05	0.66	0.997
pH = 4.37	0.99	0.03	0.994	0.06	0.54	0.999
pH = 5.97	0.77	0.10	0.995	0.13	0.36	0.984
pH = 7.44	0.88	0.11	0.980	0.15	0.36	0.993
pH = 7.53	0.82	0.11	0.973	0.15	0.37	0.995
pH = 8.13	0.88	0.13	0.984	0.17	0.34	0.986
pH = 3.69→7.00	5.44	0.14	0.988	1.05	0.41	0.987
pH = 4.37→7.00	2.77	0.28	0.986	0.64	0.35	0.984
pH = 5.97→7.00	1.22	0.16	0.980	0.27	0.35	0.989
pH = 7.44→7.00	0.73	0.09	0.956	0.12	0.39	0.991
pH = 7.53→7.00	1.00	0.05	0.925	0.11	0.46	0.980
pH = 8.13→7.00	−4.03	0.00	0.946	0.02	0.90	0.944

Q_o: maximum adsorption capacity; k_L: Langmuir constant; k_f: Freundlich adsorption constant; $1/n$: intensity of adsorption or affinity.

concentration decreased greatly from 2 to 80 mg L^{-1} after adsorption to below 1 mg L^{-1} (Fig. 3).

3.3. KCl-extractable ammonium

The proportion of KCl-extracted ammonium for biochars with an initial addition of 5, 10 and 50 mg NH_4-N L^{-1} without pH adjustment ranged from 34% to 99% of ammonium undesorbed by the two preceding water extractions. This was with a proportion of 45–89% similar to the KCl extraction, when the pH was adjusted (Fig. 4). With decreasing pH, more ammonium was extracted irrespective of pH adjustment.

3.4. Residual ^{15}N recovery and total ammonium recovery

Based on the addition of 50 mg NH_4-N L^{-1}, the proportion of ammonium remaining in the biochar after all three desorption steps was less than 5% of the amount initially adsorbed, using ^{15}N measurements (Fig. 5). This proportion decreased from 4% to 0.3% with greater oxidation, if the pH was not adjusted (Fig. 5a), but increased from 2% to 5% with greater oxidation when all biochar were adjusted to a common pH of 7 (Fig. 5b).

The total recovery of originally adsorbed ammonium in all three extractions plus any remaining ammonium in the biochar (the latter analyzed by ^{15}N isotope measurements of the solid biochar) was 61–100%, irrespective of pH adjustment (Fig. 5). A higher total recovery of adsorbed ammonium was found at greater oxidation, irrespective of pH adjustment. Without pH adjustment (Fig. 5a), when less ammonium was extracted by the three extractions at lower oxidation and higher pH, more residual ^{15}N was recovered in solid biochars. However, this greater recovery in the solid biochar after all extractions did not compensate for the unextracted ammonium and up to 39% of the originally adsorbed ammonium was not accounted for at the lowest oxidation (pH 8.13 in Fig. 5a). In contrast, when the pH was adjusted to 7, the recovery of adsorbed ammonium in the biochar after all extractions increased with greater oxidation. But again, at low oxidation (pH 8.13→7 in Fig. 5b), the total recovery in all desorption steps and biochar was lowest (with 70% of originally adsorbed), ammonium leaving 30% unaccounted.

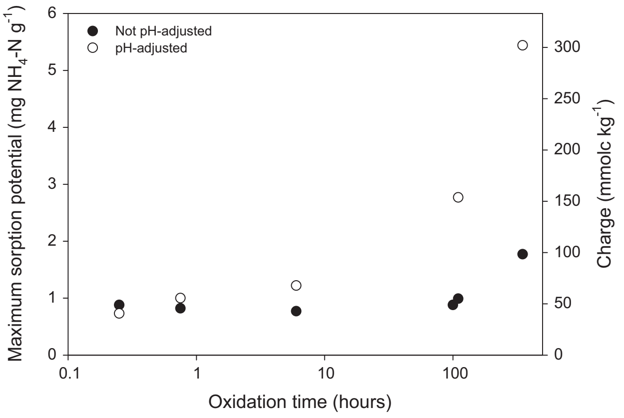

Fig. 2. Relationship between (left axis) the amount of maximum sorption capacity (Q_o from Table 2) or (right axis) the calculated charge (from the amount) and oxidation time, only shown for biochars with pH adjusted to 7.

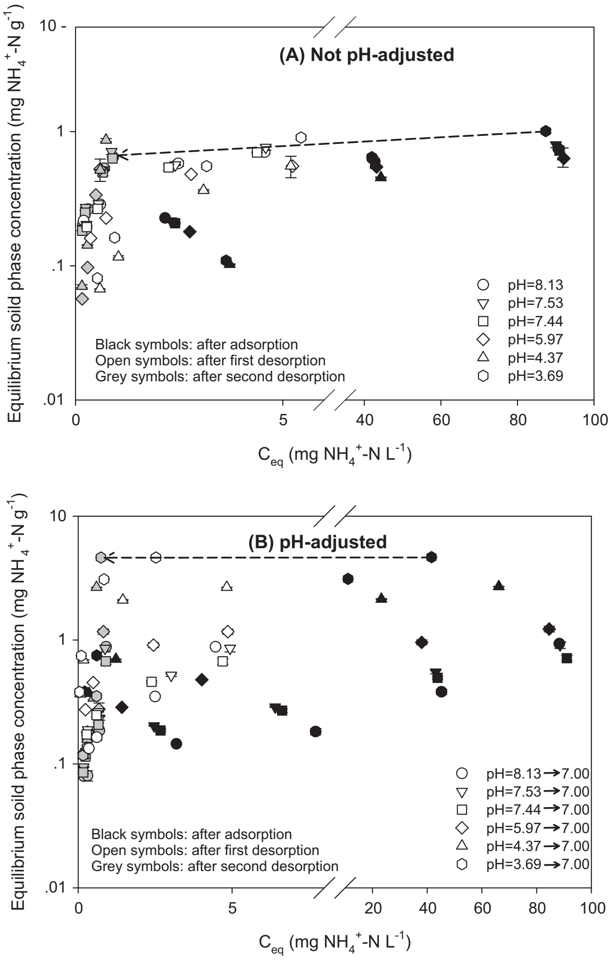

Fig. 3. Adsorption (black symbols) and the first (open symbols) and second desorption (gray symbols) isotherms of ammonium nitrogen for biochars either not pH-adjusted (A) or pH adjusted (B). Dashed line and arrow denotes the change from equilibrium concentrations after adsorption to equilibrium concentrations after the second desorption (shown only for the highest concentration). Error bars represent standard error of triplicate samples ($n = 3$). Symbols may cover error bars. C_{eq} is the equilibrium concentration of ammonium in aqueous solution (mg NH_4^+-N L^{-1}).

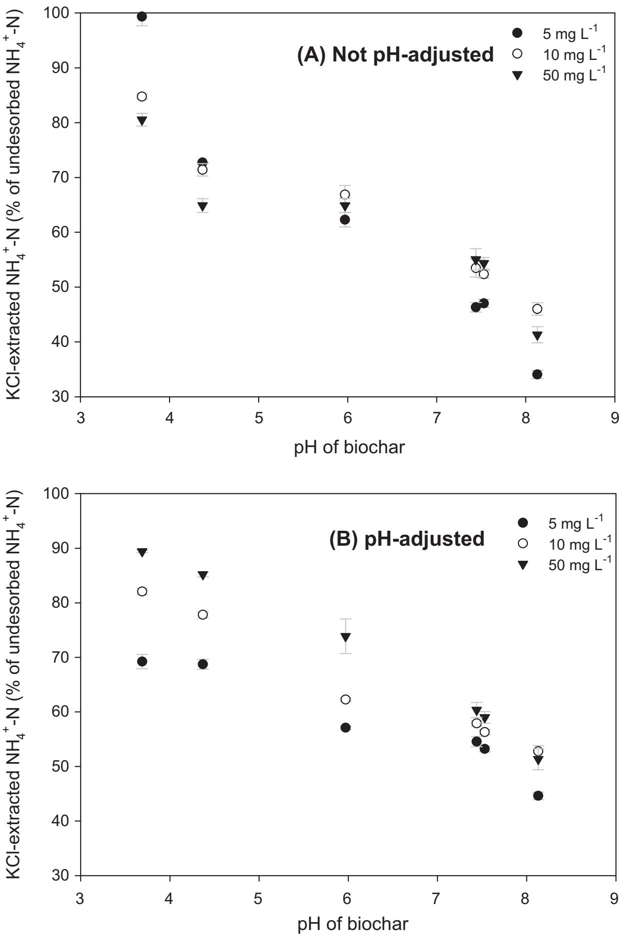

Fig. 4. Extracted ammonium using KCl as a proportion of adsorbed ammonium not being desorbed by water for biochars either not pH-adjusted (A) or pH-adjusted (B) only for initial addition of 5, 10, and 50 mg NH_4-N L^{-1}. Error bars represent standard error of triplicate samples ($n = 3$). Symbols may cover error bars.

4. Discussion

4.1. Oxidation and pH effects on ammonium adsorption

The fact that ammonium adsorption did not increase with greater oxidation when the pH was not adjusted, can be explained by competition with other cations at the exchange sites. This conforms with a common observation that protons, aluminum, reduced iron and other metals dominate the exchange sites at very low pH values (Sarkhot et al., 2013), which is not restricted to biochars but occurs for any variable charge OH surface functional groups (Brady and Weil, 2008). Even relatively carbon-rich wood-based biochars as those investigated here, possess appreciable amounts of ash (1.7%) which contain metals (Enders et al., 2012).

On the other hand, adjusting the pH to a common pH of 7, showed a significant increase in adsorption with increasing oxidation, as is commonly observed for variable-charge exchange sites (Brady and Weil, 2008). The reason for this is that after the pH adjustment, carboxyl and phenolic groups were deprotonated as well as free aluminum and iron precipitated as oxides and the negatively charged organic functional groups become the main adsorption sites for ammonium (Brady and Weil, 2008).

Abiotic oxidation with peroxide in our study generated with 302 mmolc kg^{-1} (highest value in Fig. 2) a 50% greater negative surface charge than a biotic incubation (done by Cheng et al. (2008)) of hardwood biochar (produced in a traditional charcoal kiln at appr. 500–600 °C) at 70 °C for one year with 201 mmolc kg^{-1} (both values adjusted to pH 7). However, the charge produced here with peroxide is still significantly below that found for aged biochars from residues of charcoal making after 130 years that showed on average 1644 mmolc kg^{-1} (Cheng et al., 2008), and much lower than the 15,000 mmolc kg^{-1} calculated for the pyrogenic carbon fraction in Amazonian Anthrosols (Liang et al., 2013). Therefore, natural aging processes over long periods of time are more effective in creating negative surface charge on biochar than the chemical oxidation used here. In the future, it would be useful to evaluate whether longer oxidation could generate biochars with greater surface charge.

4.2. Reversibility of ammonium adsorption with oxidation

Compared with the ammonium adsorption in water, the ammonium desorption in water was very low, which accounted for less than 27% of adsorbed ammonium for not pH-adjusted biochar and less than 16% for pH-adjusted biochar (Fig. 5). This indicated

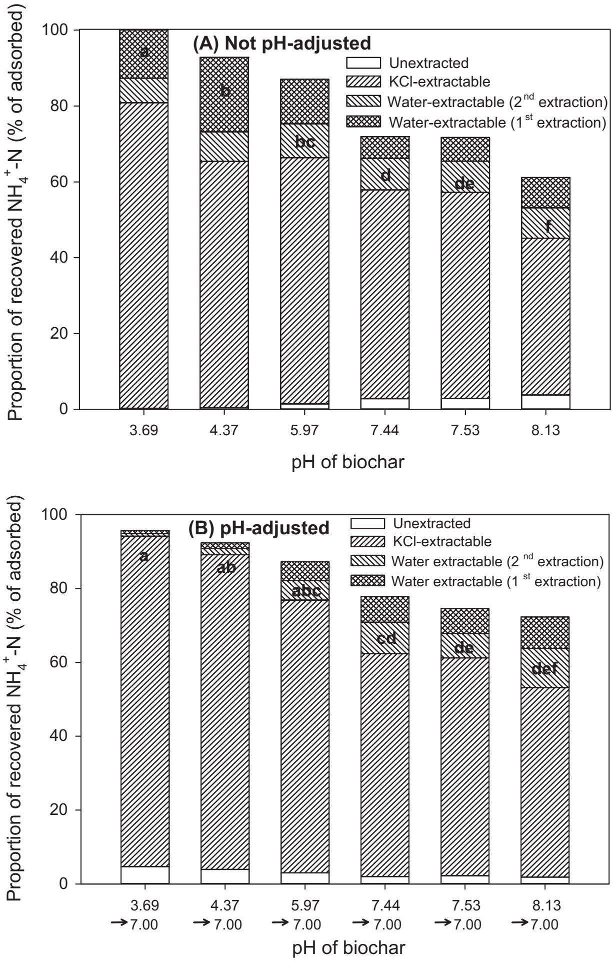

Fig. 5. Proportion of recovered ammonium in relation to pH values (with biochars either not pH-adjusted or pH-adjusted) after oxidation only for biochars with an initial addition of 50 mg NH_4-N L^{-1}. Unextracted ammonium indicates ammonium remaining in the biochar quantified by ^{15}N isotope analysis. Difference to 100% indicates missing ammonium (and likely lost by ammonia volatilization). Different small letters denote significant differences for total recovery at $P < 0.05$ ($n = 3$). Error bars are smaller than line thickness. (individual data shown in Supplementary Online Table S3).

that either pH-adjusted biochar or pH not-adjusted biochar have significant retention potential.

The nearly complete recovery of the remaining (after both water extractions; Figs. 4 and 5) adsorbed ammonium by KCl at low pH conforms with expectations that cation adsorption to organic matter and thereby also biochar is readily reversible by ion exchange (Clough et al., 2013). At lowest oxidation (irrespective of pH adjustment), however, KCl extraction only recovered another 41–89% of previously adsorbed ammonium. Since this ammonium was not found in the biochar after extraction (using ^{15}N), this incomplete recovery of adsorbed ammonium in the biochar after all extractions at higher pH could be explained by NH_3 volatilization losses, which occurs at pH values above 7 (Brady and Weil, 2008). This nearly 40% of unrecovered ammonium likely due to ammonia volatilization (at low oxidation and thereby high pH; Fig. 5) could provide a reason for why other studies also found an incomplete recovery with KCl (Saleh et al., 2012; Taghizadeh-Toosi et al., 2012; Sika and Hardie, 2014; Zhao et al., 2014). Our study therefore suggests that this often observed incomplete extraction using KCl may not be a result of strong bonds to biochar surfaces that would make adsorbed ammonium unavailable to plants. It is less likely that this loss will also be observed in soils that have a neutral or acid pH, because any pH increase of typically low biochar application rates would be buffered.

5. Conclusions

From the current work, we can conclude that ammonium adsorption is not fully reversible in aqueous solution, but fully reversible with ions and therefore exchangeable. The adsorption capacity is largely affected by oxygen-containing surface functional groups and pH as expected from previous knowledge about organic matter. The reason why ammonium adsorbed to weakly oxidized or unoxidized biochars was not found in the KCl extract may be explained by prior ammonia volatilization, and not by irreversible adsorption of the ammonium, because little (less than 5%) residual ammonium was found in the biochars after KCl extraction. The greater functionalization and therefore cation retention observed here with H_2O_2 than with biotic oxidation observed in other studies may suggest the utility of chemical oxidation for practical applications, under suitable business models. This would need to include neutralizing the acidity, since ammonium retention was minimal at low pH. Further studies including soils are necessary to explore the influence of either soil minerals or organic matter which may modify the effects seen here.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.05.062.

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