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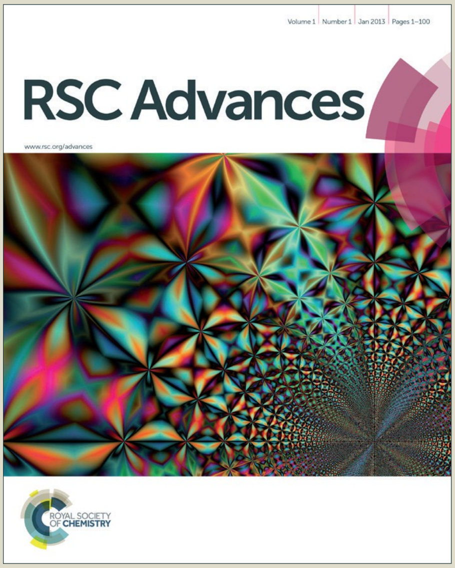

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Ammonium retention by oxidized biochars produced at different pyrolysis temperatures and residence times

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Abstract

In order to investigate the effects of pyrolysis conditions and oxidation on the retention potential of ammonium by biochar in aqueous solution, biochars were produced from mixed maple wood at different pyrolysis temperatures (300, 400, 500, 600, 700°C) and residence times (5, 60, 120, 400, 800 min) and adsorption and desorption was determined. Hydrogen peroxide was used to oxidize the biochars to pH values ranging from 7.6 to 2.7, with one set being adjusted to a pH of 7 afterwards. Without oxidation, varying either pyrolysis temperatures or residence times did not have a relevant effect on ammonium adsorption. When oxidized, however, ammonium adsorption was up to 3.6 and 1.6 times greater at lower than higher pyrolysis temperatures and shorter than longer residence times, respectively. Neutralizing the oxygen-containing surface functional groups on oxidized biochar to pH 7 further increased ammonium adsorption three to four-fold for biochars originally at a temperature of 500°C and residence time of 5 min, but did not change adsorption of biochars pyrolyzed at 600°C and above and residence time at 400 min and above. Adjusting the pH of unoxidized biochars had no effect on ammonium adsorption. Both pyrolysis temperature and residence time significantly influence the way oxidation changes charge properties with respect to ammonium adsorption by woody biochar.

Keywords: Biochar; Biomass; Slow pyrolysis; Adsorption; Ammonium nitrogen

1. Introduction

Agricultural non-point source pollution caused by large amounts of nitrogen fertilizers being used with low use efficiency has become a prominent problem which constrains sustainable agricultural development, since a significant portion of fertilizer N is lost from agricultural fields by leaching. [1] 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. [2] 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. [3, 4]

Recently, interest in biochar as a soil amendment has steadily increased and biochar has attracted wide research interest. Biochar has been touted as a soil amendment to improve degraded soils and increase agronomic yield by potentially changing the soil pH, cation exchange capacity (CEC), reducing leaching of nutrients, and supplying nutrients to plants. [5-8] Various pyrolysis conditions can result in biochars with different physical and chemical properties, nutritional and agricultural value. Among all these factors, biochar pyrolysis temperature and residence time have been considered to be the greatest overall factors that influence the final characteristics of biochar, such as porous structure, specific surface area and adsorption capacity as well as the retention of nutrients. [9-12]

A lot of research has been carried out to study the effects of pyrolysis condition on the quality and properties of biochar. [10, 13-17] Although several studies have investigated the adsorption of ammonium, phosphate and nitrate of different biochars, [18-20] few research has been conducted with regard to the oxidation effect on ammonium adsorption of biochar having different properties. Some studies found that biochar can be used for recovering excess nitrogen [20] and slowly release essential nutrients to soil in order to improve agricultural properties, [19] improve N use efficiency, [21] and reduce leaching losses of N.[22] Key chemical and physical properties of biochar are greatly affected both by choice of feedstock and process conditions (mainly temperature, residence time, heating rate and feedstock preparation). These properties affect the interactions of biochar with the soil as well as its fate in the environment. This underlines the importance of evaluating the effect of pyrolysis conditions on the nitrogen retention potential before land application.

Biochar is expected to be highly oxidized after long-term exposure to natural oxidation processes through the formation of oxygen-containing functional groups which can increase the surface acidity and CEC, [23-26] which influences the nutrient retention capacity of biochar. Ammonium retention by biochar may be readily explained by electrostatic adsorption to negatively charged surface functional groups. [19, 24] However, there has been little experimental evidence that this oxidation can be replicated by short-term abiotic oxidation in the laboratory under different pyrolysis conditions, which may inform post-production manipulation of biochars. In addition, it is unclear whether the adsorption found with aged biochars in soil is influenced by pyrolysis conditions. Therefore, in order to develop a framework for the selection of biochars, the effects of pyrolysis temperature and residence time on ammonium nitrogen retention by oxidized biochar from aqueous solution need to be better understood.

The objectives of this study were to: (1) examine the retention potential of ammonium by biochars that have been oxidized to different extents; (2) establish the optimum pyrolysis temperature and residence time at which oxidized biochars adsorb the most ammonium in aqueous solution.

2. Experimental methods and materials

2.1 Preparation of biochar

Maple wood biochars (20% sugar maple, 80% red maple) which were pyrolyzed at 300, 400, 500, 600, 700°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}. Another batch of maple wood biochars was pyrolyzed at 500°C with residence times of 5 min, 30 min, 60 min, 120 min, 400 min and 800 min. The physical and chemical properties of biochars are shown in Table 1. [27] All feedstocks were dried at 60°C to ca. 10% moisture (w/w) prior to pyrolysis. The glassware and PE centrifuge tubes were acid washed in a hydrochloric acid bath (10%) and rinsed with deionized (DI) water before use. The biochars were oxidized by using H_2O_2 (30% v/v) for two weeks at 30°C, all using a solid-to-liquid ratio of 1:10 (w/v), which we found to result in significant changes in surface charge of biochar produced at 500°C for 30 min (Wang et al., 2015). H_2O_2 was chosen in order to minimize precipitation, complexation or analytical interference which have been observed with other oxidants (e.g., H_2SO_4, HNO_3). [28] After oxidation, the H_2O_2 was removed by filtration under suction using a Büchner funnel, fitted with Whatman No.1 filter paper, attached to a Büchner flask connected to a Welch Duo-Seal 1400 vacuum pump and the oxidized biochars were rinsed with DI water. The pH values of biochars were determined using a glass electrode (detection limit is 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). After determining the initial pH values of the oxidized biochar samples, the biochars were dried under 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 pH values were adjusted every 24 h until they reached equilibrium, then suspensions were filtered through Whatman No.1 filter paper.

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. Determination of the CEC of biochar is based on the method by Page. [29] Elemental H, O, C 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. [16]

2.2 Adsorption experiments

Batch adsorption experiments were conducted in PE centrifuge tubes at room temperature. All adsorption experiments were performed in triplicate. 0.5 g of biochar was added into 50-mL centrifuge tubes containing 40 mL of ammonium sulfate solution with 100 mg NH_4–N L^{-1}. The tubes were shaken at 400 rpm in a mechanical shaker for 16 h and then centrifuged at 2500rpm for 10 min, and the supernatant was carefully aspirated using a Pasteur pipette. Ammonium N concentrations in the supernatant were 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 a continuous flow analyzer (Bran and Luebbe Autoanalyzer, SPX, Charlotte, NC).

2.4 Statistical analysis

The results of adsorption and desorption experiments were the average of three replications. The statistical software package SPSS 13.0 (Chicago, IL, USA) was used for descriptive statistics, ANOVA testing (post-hoc LSD analysis at $p < 0.05$) of ammonium adsorption and desorption at different pyrolysis temperatures and residence times. In order clarify the data present in Table 1, we performed regression analyses and added p values into the table.

3. Results

3.1 Biochar properties

Increasing the pyrolysis temperature had great effects on proton activity due to decreases in acid functional groups with greater pyrolysis temperature. Fresh biochar pH values ranged from 6.94 at 300°C to 10.20 at 700°C. Biochars produced at higher temperature had high alkalinity, and those at lower temperature had lower alkalinity. After oxidation, the pH dropped to 2.87 and 2.69 for biochars produced at 300°C and 400°C, respectively (Fig. 1a). During pH adjustment using NaOH, all of the oxidized biochars produced at these low temperatures dissolved, and no adsorption and desorption data could be obtained. This may be explained by the reaction between sodium hydroxide and acidic functional groups, such as phenolic hydroxyl and carboxyl groups. In contrast to the low-temperature biochars, oxidation had lower effects on pH decrease for biochar produced at higher temperature. After oxidation of biochar produced at 700°C, pH values dropped from 10.2 to only 7.63.

In contrast to pyrolysis temperature, increasing the residence time from 5 min to 800 min at 500°C had no significant effect on pH values of the unoxidized biochar, which ranged from 8.82 at 5 min to 9.08 at 800 min (Fig. 1f). Interestingly, oxidation significantly reduced the pH of biochars with short residence times, but had little effect on pH of biochar pyrolyzed for 400 min or longer. When oxidized, varying the residence time from 5 min to 80 min at a pyrolysis temperature of 500°C had almost identical effects on pH as varying the pyrolysis temperature from 300°C to 700°C at a residence time of 30 min. This may be explained by the aromatization level of biochar. The high temperature and long residence time makes the carbon highly aromatic.

Ash contents significantly increased with higher pyrolysis temperature and residence time. In contrast to ash, volatile contents decreased significantly with higher pyrolysis temperature, when the residence time increased from 60 min to 800 min, the change of volatile contents was not obvious. Fixed carbon contents of biochars significantly increased with increasing pyrolysis temperature, but no significant increase was observed when prolonging pyrolysis. The surface area also increased significantly with increasing pyrolysis temperatures, but there was no alteration when pyrolyzed continuously at 500°C. Both pyrolysis temperature and residence time had significant effects on the CEC of biochar. With the increase in pyrolysis temperature, the CEC of biochar decreased from 117.15 cmol kg^{-1} to 47.11 cmol kg^{-1}. Total C contents increased while total H and O decreased with increasing temperature (Table 1).

Biochar yields decreased with increasing pyrolysis temperatures and residence times Increasing the pyrolysis temperature resulted in a significant decrease in biochar yield, and the highest yield was obtained at a temperature of 300°C. For instance, the yield of biochar at 300°C was 62% of the dry feedstock, while at 400°C, the yield decreased to 32% of the dry feedstock. At temperatures of 500, 600 and 700°C, the yield of biochar was reduced to 27%, 26% and 24% of the initial weight, respectively (Fig. 1b). The largest yield loss occurs within the first 120 min of residence time during pyrolysis. Increasing the residence time from 120 min to 800 min decreased the biochar yield only slightly (Fig. 1g).

3.2 Ammonium adsorption

In general, fresh biochars had lower ammonium adsorption capacity than oxidized biochars; when oxidized, pH-adjusted biochars had higher adsorption capacity than not pH-adjusted biochars; and oxidized and pH-adjusted biochars pyrolyzed at lower temperatures or for shorter period of residence times had higher adsorption capacity than those pyrolyzed at higher temperatures or for longer period of times. For the fresh biochars, there was no relevant difference among different pyrolysis temperatures. The adsorbed ammonium for the fresh biochars at 300°C and 400°C was 0.87 mg g^{-1} and 0.58 mg g^{-1}, respectively, and for those pyrolyzed at 500°C, 600°C, 700°C 0.52 mg g^{-1}, 0.46 mg g^{-1}, and 0.46 mg g^{-1}, respectively (Fig. 1c). When oxidized, biochars pyrolyzed at lower temperatures (300°C, 400°C) had higher adsorption capacity than those at higher pyrolysis temperatures (500°C, 600°C, 700°C). After the pH adjustment, ammonium adsorption significantly increased at lower pyrolysis temperatures (≤500°C), but did not change for higher pyrolysis temperatures (≥600°C).

There was no significant difference in ammonium adsorption for fresh biochars among different residence times. However, neutralizing the oxygen-containing surface functional groups on oxidized biochars to pH 7 increased ammonium adsorption two to three-fold for biochars pyrolyzed from 5 min to 120 min (Fig. 1h).

3.3 Ammonium desorption

In general, ammonium desorption with lower pyrolysis temperature and shorter pyrolysis times was higher than with higher temperature and longer times (Fig. 1d and i). pH adjustment significantly affected the recovery: non-desorbed ammonium remained near 100% if the pH was adjusted, but decreased to 80% if the pH was not adjusted, irrespective of oxidation (Fig.1e and j). Oxidation did not have a discernable effect on the proportion of desorbed ammonium.

4. Discussion

4.1 Effect of oxidation and pH on ammonium retention

Freshly produced biochars typically have very low ability to adsorb ammonium, showing low cation exchange capacity. [30] The increase in ammonium adsorption through oxidation by H_2O_2 corroborate the observations from naturally aged charcoals [23] and incubation studies.[24] The unchanged ammonium adsorption despite greater oxidation without pH adjustment may be explained by protons and possibly aluminum and reduced iron or other metals that dominate the exchange sites at very low pH values.[20] Even carbon-rich wood-based biochars as those investigated here, possess appreciable amounts of ash (1.7%) which contain metals.[16] On the other hand, adjusting the pH to a common pH of 7, significantly increased adsorption with increasing oxidation which corroborate the observations from our previous work.[31] The reason for this is that after the pH adjustment, the carboxyl and phenolic groups were deprotonated as well as free aluminum and iron may have precipitated as oxides and the negatively charged organic functional groups became the main adsorption sites for ammonium.

Abiotic oxidation with peroxide generated oxygen-containing functional groups, which largely improve ammonium adsorption capacity. Another reason for the enhancemed ammonium adsorption capacity is the increase of negative charges on the surface of the biochar. [31] Higher pyrolysis temperatures and longer residence times result in higher degrees of biochar aromaticity. Elemental H/C and O/C ratios can be used to estimate the degree of aromaticity of the carbon structure. Biochars produced at low temperatures had higher H/C ratios, and biochars produced at high temperatures had lower H/C ratios. Previous studies have shown that biochar amendment can increase CEC in soil [32] and that when aging and weathering of the biochar occurs the CEC can be further increased. [33] Therefore, the oxygen-containing functional groups and negative charges in the oxidized biochar pyrolyzed under low temperatures and short residence times are higher than those pyrolyzed under high temperatures and long residence times. Previous studies have also pointed out that, initially, biochars produced at high pyrolysis temperatures (800˚C) had greater exchangeable cations and CEC than those produced at lower temperatures. However, after 8 weeks of oxidation the CEC of low temperature biochars was significantly higher, [34] which is consistent with the results of this study.

4.2 Pyrolysis conditions and ammonium nitrogen retention

Without oxidation, varying the pyrolysis residence time beyond 5 min had no effects on ammonium adsorption, corollary with a lack of change in pH, elemental ratios, or surface area. The lack of an increase in surface area may be explained by the observation that prolonging heat treatment at 500°C may lead to increased softening of some volatile fractions, forming an intermediate melt which closes and seals off some of the pores, compensating for any creation of pores with longer pyrolysis times.

However, the lack of change in ammonium adsorption to unoxidized biochars as a function of pyrolysis temperature is more difficult to explain, as pH, O/C ratios, and surface areas suggested a change in biochar properties. It is possible that the decrease in acid functional groups with increasing pyrolysis temperatures is compensated by an increase in surface area, canceling any temperature effects for the biochars studied here. Increases in surface area with higher pyrolysis temperature are typically observed, [14] as are lower O/C ratios. [16]

Interestingly, when biochars were oxidized, both residence time and pyrolysis temperature affected ammonium adsorption, and did so to a much greater extent than if they were not oxidized. The much greater adsorption to oxidized biochars produced at lower temperatures and shorter residence times may be the result of greater oxidation, shown by a greater pH drop and increases in the O/C ratios. Greater oxidation with shorter pyrolysis times and lower temperatures upon exposure to H_2O_2 may be explained by the lower degree of fused aromatic C structures typically found under those conditions,[35, 36] also indicated by the higher H/C ratios found in our study. This probably also means that those biochars produced at lower temperatures and shorter residence times will develop cation retention capacity more quickly when added to soil. This may pose a tradeoff with an intent to produce biochars with long turnover times in soil, which are typically produced at higher pyrolysis temperatures.[37]

5. Conclusions

Freshly produced biochars have low ability to adsorb ammonium. Only pyrolysis temperature but not residence times affected oxidation, pH, surface area, and yield of fresh biochar, but none of the two affected the adsorption capacity of fresh biochar. Short-term abiotic oxidation significantly increased ammonium retention of biochars, and under these oxidized conditions, also pyrolysis residence times had significant effects. The greater ammonium adsorption for less pyrolyzed biochars when oxidized may constitute a tradeoff with maximizing biochar persistence where both are desired. Future research should examine whether this also holds for effects of pyrolysis residence times on biochars oxidized over time when they are added to soils.

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Table 1. Physical and chemical properties of biochars.

Process conditions		pH	Proximate analysis (wt.% dry)			Elemental contents					Surface area (m^2 g^{-1})	
Pyrolysis temperature (°C)	Residence time (min)		Volatile matter	Ash content	Fixed carbon	C_{tot} (w%)	H （w%）	O (w%)	H/C_{tot} (mol mol^{-1})	O/C_{tot} (mol mol^{-1})	BET CO_2	CEC (cmol kg^{-1})
Original biochar												
300	30	6.94	68.5	0.54	31.0	58.9	5.22	32.9	1.06	0.42	72.4±1.5	117.2±2.3
400	30	7.60	30.3	1.75	67.9	78.8	3.53	17.0	0.54	0.16	182±1.9	98.6±1.6
500	30	8.90	21.1	2.16	76.7	91.5	2.81	9.51	0.37	0.08	250±2.0	78.1±1.4
600	30	9.09	13.4	2.29	84.3	88.9	2.34	5.56	0.32	0.05	298±2.0	72.5±0.9
700	30	10.2	8.44	2.59	89.0	94.9	1.33	3.92	0.17	0.03	337±2.1	47.1±0.7
P-value		0.003	0.034	0.029	0.034	0.042	0.005	0.023	0.027	0.049	0.004	0.002
500	5	8.82	24.3	1.65	74.0	83.3	2.98	11.9	0.43	0.11	222±2.0	122.7±1.8
500	60	8.84	18.5	1.93	79.6	88.8	2.89	9.18	0.39	0.08	266±2.1	114.1±1.1
500	120	8.67	17.7	2.04	80.2	86.2	2.79	8.23	0.39	0.07	272±2.1	104.1±0.7
500	400	8.70	14.5	2.34	83.2	91.6	2.67	7.96	0.35	0.07	294±2.1	93.0 ±0.6
500	800	9.08	14.4	2.58	83.0	84.5	2.54	7.06	0.36	0.06	274±1.9	70.7±0.4
P-value		0.227	0.129	0.016	0.150	1.000	0.013	0.140	0.133	0.169	0.355	0.004
Oxidized biochar												
300	30	2.87	-	-	-	49.4	5.23	44.3	1.27	0.67	61.5±1.9	143.2 ±1.9
400	30	2.69	-	-	-	59.5	3.03	34.6	0.61	0.44	132±1.8	125.8 ±1.5
500	30	4.01	-	-	-	73.4	2.80	19.7	0.46	0.20	243±2.0	122.7±1.6
600	30	7.00	-	-	-	84.0	2.02	8.36	0.29	0.07	287±1.9	117.8±2.1
700	30	7.63	-	-	-	93.3	1.32	5.33	0.17	0.04	319±2.0	110.9±2.8
P-value		0.017				0.000	0.015	0.003	0.024	0.008	0.004	0.013
500	5	3.10	-	-	-	67.3	2.53	25.6	0.45	0.28	174±1.8	131.4±3.1
500	60	3.94	-	-	-	76.2	2.61	18.6	0.41	0.18	246±1.9	124.6±2.9
500	120	4.45	-	-	-	77.1	2.50	15.8	0.39	0.15	255±2.0	113.4±1.4
500	400	7.12	-	-	-	80.5	2.47	12.6	0.37	0.12	267±1.9	96.7±1.1
500	800	6.99	-	-	-	83.4	1.95	10.1	0.28	0.09	269±1.9	84.9±0.7
P-value		0.046				0.089	0.021	0.074	0.007	0.104	0.251	0.011

a Ctot is the total carbon of biochar.

b P-value for a linear regression of the effect of pyrolysis temperature and residence time.

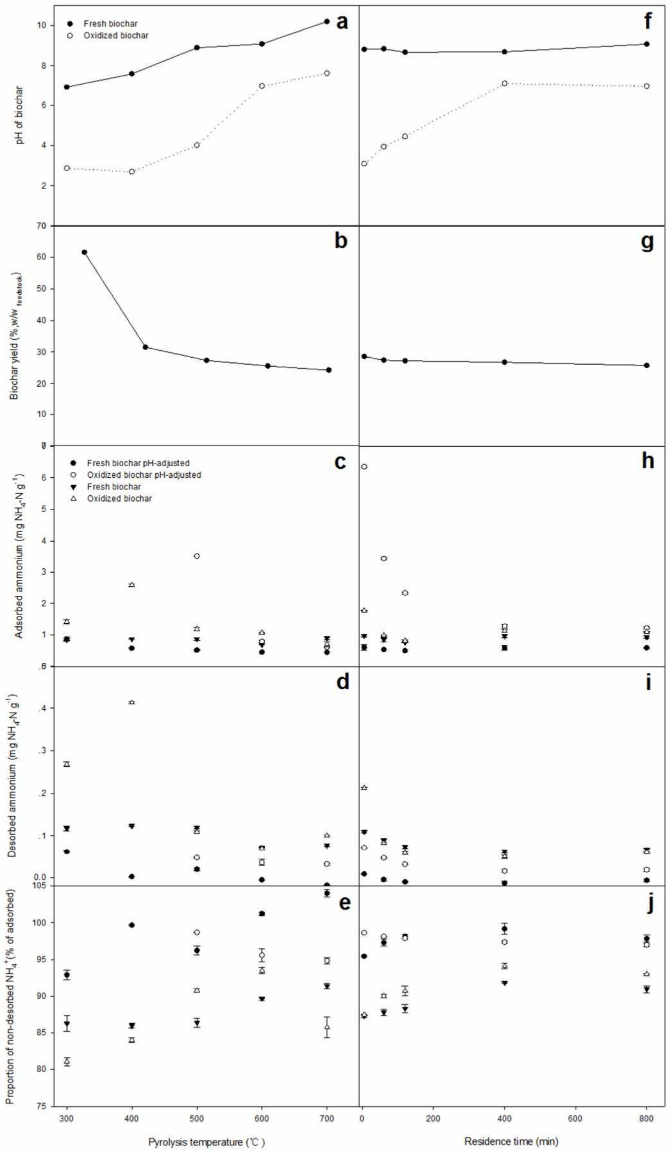

Fig. 1. The effect of pyrolysis temperature (a-e) or residence time in the pyrolyser (g-j) on pH, biochar yield, ammonium adsorption, ammonium desorption and the proportion of non-desorbed ammonium (adsorption and desorption of oxidized and pH-adjusted biochars at low temperatures could not be studied due to their high solubility). Error bars represent standard error of triplicate samples (n = 3). Symbols may cover error bars.
171x295mm (150 x 150 DPI)