PZNC ~9-10

biomass + AlCl_3

pyrolysis @ 700 °C

ALUMINUM AND IRON BIOMASS PRETREATMENT IMPACTS ON BIOCHAR ANION EXCHANGE CAPACITY

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Abstract

Some biochars have significant anion exchange capacity (AEC) under acidic pH conditions but typically have little or no AEC at neutral to alkaline pHs. We hypothesized that metal oxyhydroxide surface coatings on biochar will increase biochar anion exchange capacity (AEC) at higher pHs by virtue of the high point of zero net charge of metal oxyhydroxides. Here we report that pyrolysis temperature and the distribution of metal oxyhydroxides in biochars prepared by slow pyrolysis of biomass pre-treated with Al or Fe trichlorides strongly influenced biochar AEC. Biochars produced at 700 °C exhibit greater AEC than biochars similarly prepared at 500 °C. Spectroscopic (*FTIR*, *XPS*, and *SEM-EDS*) studies provided evidence for the formation of Al-O-C organometallic moieties on biochar surfaces that formed during pyrolysis. To a lesser extent, Fe also formed Fe-O-C surface structures on biochar, but most Fe was present in discrete crystalline phases ranging from zerovalent iron to ferric oxides. These organometallic bonding structures are a means of supporting metal oxides on biochar carbon and are responsible for broader metal atom distributions, which can increase AEC through the development of metal oxyhydroxide surface coatings that exhibit high points of zero net charge.

1. Introduction

Pyrolysis-based bioenergy production (PBBP) is under development to provide sustainable energy in the wake of climate change and our degrading environment. Biochar is the solid residue of pyrolyzed materials, thus is a co-product of this emerging technology and has attracted substantial interest as a means to sequester atmospheric carbon (C) in soil in an effort to help mitigate climate change [1,2]. Most research has focused on use of biochar as a soil amendment to modify soil properties for agricultural and horticultural applications as an industrial PBBP system would generate large amounts of biochar. Biochar has also been investigated for greener, more sustainable applications to meet societal needs for adsorbents in waste water treatment [3,4], heterogeneous catalysis [5,6], and as an alternate to activated carbon [7,8]; illustrating the potential for this carbon-based material to serve in a broad spectrum of applications.

Myriad environmental and water quality problems are associated with anionic contaminants. Extensive leaching of nutrient anions, nitrate and phosphate, from soil is due to the lack of anion exchange capacity in most temperate region soils. Eutrophication of open waters due to nitrate and phosphate leaching from agricultural soils is responsible for hypoxia in the Gulf of Mexico with similar hypoxic conditions observed in coastal waters of China and other parts of the world. Some heavy metals, metalloids, and non-metals such as arsenic, chromium, and selenium are oxidized in soil environments forming oxyanions, which may contaminate surface and ground water posing serious health risks. Organic acids and sulfonate compounds originating from natural organic carbon in soil and personal care products in sewage are poorly removed by activated carbon, adding challenge to municipal water production and wastewater treatment. Biochar with significant anion exchange capacity (AEC) can potentially be used to remediate

contaminated soil and to remove problematic anions from water; however biochar AEC is limited under neutral and alkaline conditions [9].

We have previously identified three types of functional groups on biochar surfaces that contribute to AEC⁹: (1) oxonium (O^+) heterocycles; (2) N heterocycles (pyridinium groups); and (3) condensed aromatic carbon, which may acquire positive charge by abstracting protons from aqueous solutions. Both pyridinium groups and the abstraction of protons by condensed aromatic carbon are pH dependent sources of positive charge and are anticipated to contribute negligible surface charge under neutral and alkaline conditions [9]. Oxonium heterocycles, by contrast, are a source of pH-independent AEC; however, non-bridging oxonium groups are subject to nucleophilic attack by OH^- and rapidly degrade under alkaline conditions [10]. Hence, most biochars exhibit little AEC under neutral to alkaline conditions, the latter contributing to the lability of AEC at high pH conditions.

We hypothesize that biochar AEC can be increased through surface modification with metal oxyhydroxides. Metal oxyhydroxides such as those of aluminum (Al) and iron (Fe) are dominated by pH-dependent surface charge with relatively high points of zero net charge (PZNC). Indeed, $\gamma-Al_2O_3$ and $\gamma-Fe_2O_3$ (maghemite) have PZNCs at pHs 8.1 and 8.8, respectively [11,12]. Biochar-metal oxide composites have been previously prepared by pyrolysis of biomass pretreated with soluble Fe salts, which resulted in formation of magnetite and $\gamma-Fe_2O_3$ phases distributed on biochar surfaces [13,14]. These composites were stable during adsorption studies and demonstrated that the Fe oxide phases remained fixed on biochar surfaces, alluding to potential bonding between biochar C and Fe oxides. Evidence of Fe-N-C bonding was first reported by Widelöv (1993), who investigated Fe-carbon black composites prepared by first adsorbing Fe porphyrins on carbon black and then heating the complexes at 800

°C under an inert atmosphere [15]. These bonding structures were later demonstrated to be thermally stable up to this temperature [16]. Studies in organoaluminum chemistry have demonstrated that Al coordinates with alkyl and amine moieties [17] and that pyrolysis of iminoalane formed stable C-Al-N and C-Al bonding structures with yield promoted by allylation of Al precursors [18,19]. Thus, the literature demonstrates that bonding structures between Fe, Al and organic substrates can be created and may be stable at pyrolysis temperatures. Hence, we further hypothesized that Al and Fe may form bonding structures with biochar C during pyrolysis of biomass and that such metal-biochar composites will exhibit increased AEC and PZNC due to the presence of metal oxyhydroxide phases and surface coatings that form upon hydration of the metal oxide. In this work, we report a one-step pyrolysis method for the production of metal-biochar composites from several biomasses pre-treated with Al and Fe chlorides and the effect of these treatments and pyrolysis temperature on biochar surface chemistry and AEC.

2. Experimental

2.1 Biochar Preparation

Biochars were prepared from alfalfa meal, corn stover, and cellulose; which were wetted with FeCl₃ or AlCl₃ at 1% weight of metal to weight of biomass (500 g) using 1 M stock solutions of these metals. Additional water, up to 1 L, was added to sufficiently wet the biomass, and the resulting slurries were thoroughly mixed to uniformly distribute the metal, dried in a convection oven at 105 °C for at least one day and subsequently slow pyrolyzed using a programmable muffle furnace that heated to highest treatment temperatures (HTTs) of 500 °C and 700 °C under N₂ purge. Control biochars were produced from the same untreated biomasses. Biochars are referred to as control or Al, Fe-biochar referring to the specific metal-biomass treatment.

2.2 Biochar Characterization

Specific surface area was measured by N₂ adsorption using a Quantachrome NOVA 4200e and calculated by the BET method for relative pressures ranging 0.05 to 0.30. AEC was measured by Cl⁻ for Br⁻ compulsive exchange of 1 g biochar samples in water for which Br⁻ was assayed by ion chromatography using a Dionex[®] 1100 ion chromatograph equipped with an ASRS 300 4 mm conductivity detector. The mobile phase was 8 mM Na₂CO₃ / 1 mM NaHCO₃ and the method was run isocratically at 0.7 mL min⁻¹ using an IonPac[®] AG14A 5 µm 3 x 30 mm guard column and an IonPac[®] AS14A 5 µm 3 x 150 mm analytical column. PZNC was determined as the pH of zero salt effect using a batch method adapted from Zelazny et al. (1996) [20]. FTIR spectroscopy was performed using a Nicolet 560 Magna - IR spectrophotometer with the diffuse reflectance accessory and spectra are reported in absorbance mode. Samples were prepared by co-grinding biochar with spectroscopy grade KBr at one weight percent. XRD analysis was performed of random powder mounts of biochar using CuKα radiation generated at 40 KV and 30 mA in step scan mode with a step size of 0.05° 2θ and a dwell time of 7 seconds per step using a Siemen D5000 diffractometer. A scintillation counter detector with fixed 0.15° divergence and 1.0° anti-scattering slits was used. Data was analyzed using JADE v9.0. Elemental analysis was performed using an Elementar Vario Micro Cube combustion analyzer for C, H, N and S and complementary atomic analysis by XRF spectroscopy using a Philips PW 2404 spectrometer. XPS was performed using a Physical Electronics 5500 Multitechnique spectrometer equipped with a graphite monochromator and AlKα radiation generated at 250 W. Spectra were shifted to the carbon maximum at 284.7 eV and deconvolution was performed with Gaussian-Lorentian fit with Shirley background removed using Casa XPS v 2.3.16 PR 1.6. Mössbauer spectroscopy was performed using a conventional, constant acceleration type

spectrometer in transmission geometry with a $^{57}\text{Co}(\text{Rh})$ source at ambient temperature. The driver velocity was calibrated using $\alpha\text{-Fe}$ foil and all isomer shifts (IS) are quoted relative to the $\alpha\text{-Fe}$ foil at RT. MossA software was used to analyze the spectra [21]. SEM-EDS analysis was performed with an FEI QUANTA FEG 250 scanning electron microscope using a 10 kV beam of about 1nA. Images were collected using secondary electrons at 3000x magnification. Elemental maps were obtained by energy dispersive x-ray analysis using an Oxford Aztec EDS. More thorough description of these techniques are fully provided in the Supplemental Information.

3. Results

3.1 Anion Exchange Capacity and Surface Charge

Table 1 presents AEC, PZNCs, and specific surface area (SSA) of biochars prepared from alfalfa meal, corn stover, and cellulose. Consistent with our previous results, AEC was higher for biochar controls (no metal pretreatments) produced at 700 °C than 500 °C and AEC of biochar controls increased significantly ($p < 0.0001$) with decreasing pH (Table 1) [9]. PZNCs of controls also increased with HTT, consistent with greater oxonium heterocycle content [9] and AEC at pH 8. The 700 °C HTT biochars produced from Al-treated biomass exhibited greater AEC relative to biochar controls (except 700 °C cellulose biochar at pH 6). The AECs of the 700 °C HTT Fe-biochars were also higher than the controls at pH 8, but mixed results for these biochars were obtained at pH 4 and 6. PZNC also increased for both metal treatments relative to the controls for the 700 °C but not the 500 °C HTT biochars.

Measured SSA was influenced by HTT (700 °C > 500 °C) and feedstock (cellulose > corn stover > alfalfa), but there was no clear relationship between SSA and AEC for any of the pH levels (Table 1). SSA decreased with HTT for control biochars produced from cellulose but increased with HTT for biochars produced from corn stover and alfalfa, illustrating that SSA

varies with both feedstock and pyrolysis conditions. Thus, our results show that biochar AEC is influenced by feedstock, HTT, and metal treatments, solution pH, and surface charge, but not by surface area.

Table 1: Specific surface area, AEC, and PZNC of biochars. AEC reported as mean (standard deviation)

	HTT (°C)	Treatment	SSA (m ² g ⁻¹)	AEC (cmol kg ⁻¹) -----pH-----			PZNC
				4	6	8	
Cellulose	500	Control	321	7.84(1.74)	2.63(0.189)	0.602(0.344)	8.4
		Iron	373	5.23(0.922)	1.18(0.787)	0.306(0.0709)	3.7
		Aluminum	247	17.6(2.72)	2.90(1.21)	0.636(0.564)	5.8
	700	Control	229	24.2(5.32)	18.1(7.76)	4.11(0.166)	8.7
		Iron	331	19.4(1.15)	11.9(0.768)	8.85(2.38)	9.9
		Aluminum	305	28.0(2.46)	17.6(3.36)	15.5(5.61)	10.2
Corn Stover	500	Control	150	17.5(5.19)	3.77(0.590)	1.05(0.184)	6.0
		Iron	159	13.9(5.58)	4.39(1.28)	1.12(0.778)	5.7
		Aluminum	72	22.2(2.34)	6.18(1.38)	2.89(0.930)	7.2
	700	Control	259	27.8(8.42)	13.8(3.78)	7.19(1.24)	9.1
		Iron	263	27.6(5.18)	16.4(2.86)	9.24(2.30)	9.5
		Aluminum	309	44.0(2.80)	22.3(7.23)	11.6(1.07)	9.4
Alfalfa	500	Control	39	10.9(1.83)	3.10(0.249)	0.938(0.302)	6.5
		Iron	54	17.3(9.23)	6.69(0.817)	2.92(0.436)	3.9
		Aluminum	37	26.8(12.4)	15.2(4.17)	2.74(0.639)	7.3
	700	Control	176	25.9(3.33)	9.64(0.961)	2.15(0.711)	6.9
		Iron	262	17.3(3.19)	18.2(0.241)	10.9(2.51)	7.4
		Aluminum	298	52.9(1.87)	28.9(1.41)	23.5(4.96)	9.1

3.2 SEM-EDS Analysis

Scanning electron microscopy and energy dispersive X-ray (SEM-EDS) elemental mapping were used to investigate the distribution of Fe, Al, O, and exchangeable halides (Cl⁻ or Br⁻) on surfaces of the metal-treated biochars (Figs. 1,2,S1). Al and O were diffusely distributed on surfaces of the 700 °C HTT Al-cellulose biochar, although both elements were relatively enriched on the left side of the specimen shown in Fig. 1. The light gray shading evident on the left side of the SEM micrograph reflects the greater electron density of Al and O relative to C,

the dominant element in the cellulose biochar. The atomic distribution of Cl indicates the distribution of AEC sites on the biochar surfaces. Cl is diffusely distributed over all surfaces, but appears slightly more concentrated on the left side of the specimen where Al and O are also concentrated. A bright spot evident in the upper left hand corner of the Al and O elemental maps suggests the presence of a discrete aluminum oxyhydroxide phase. This particle is also clearly evident as a bright spot on the Cl map, indicating that this particle had higher AEC than other regions in the sample.

Fig. 1: SEM micrograph and EDS elemental maps of 700 °C HTT biochar prepared from Al^{3+} -treated cellulose.

Iron and O were present in both discrete particles and diffuse coatings on surfaces of the 700 °C HTT Fe-cellulose biochar (Fig. 2). The discrete particles are evidenced by white spots on the SEM micrograph and corresponding bright spots on the Fe and O elemental maps. Cl, which indicates the distribution of AEC sites, is associated with all biochar surfaces, but is relatively enriched along with Fe and O on a large rectangular biochar particle on the left side of the image. Cl, however, was not concentrated on the discrete particles suggesting that AEC was not exclusive to the Fe phases. By contrast, Fe was diffusely spread over surfaces of the 700 °C HTT Fe-alfalfa biochar (Fig. S1), suggesting that feedstock properties influence the formation of discrete versus diffuse Fe phases on biochar surfaces during pyrolysis.

Fig. 2: SEM-EDS micrograph and elemental maps of 700 °C HTT Fe-cellulose biochar.

3.3 XRD Analysis

X-ray diffractometry indicated the presence of sylvite (KCl) and quartz (SiO_2) in samples of 700 °C HTT biochars produced from corn stover and alfalfa meal (Figs. 3,4). Calcite (CaCO_3) was previously reported in control biochars [9], however was not detected in the Fe and Al biochars suggesting that calcite in these biochars is more amorphous and/or of smaller crystallite size. Consistent with these interpretations, elemental analysis (Table S1) revealed substantial amounts of Si, Ca, Mg, K and Cl in the corn stover and alfalfa meal biochars. The cellulose used

in this study was nearly free of ash, thus the control biochar prepared from cellulose contained low levels of inorganic elements which form crystalline phases with pyrolysis of other forms of biomass (Table S1). X-ray diffraction patterns of the 700 °C HTT biochar prepared from Al-treated cellulose displayed broad amorphous C reflections [9] maximized at approximately 23° and 45° 2 θ (Fig. 4) but no evidence of inorganic crystalline phases despite containing 2.98% Al (Table S1). The lack of Al XRD peaks suggests that Al in biochar was in amorphous forms or structures of very short-range crystalline order. Magnetite was detected in the 700 °C HTT Fe-biochar prepared from cellulose and zerovalent iron (Fe⁰) in biochar prepared from alfalfa, indicating that feedstock properties influenced Fe reduction during pyrolysis (Fig. 5).

Fig. 3: XRD patterns of 700 °C HTT biochars prepared by slow pyrolysis of Al treated biomass feedstocks. Q = quartz (SiO₂), S = sylvite (KCl).

Fig. 4: XRD patterns of 700 °C HTT biochars prepared from Fe treated biomass. Fe⁰ = zerovalent iron, Q = quartz (SiO₂), S = sylvite (KCl), M = magnetite (Fe₃O₄).

3.4 Mössbauer Spectroscopic Analysis

Mössbauer spectroscopy provided quantitative information on the oxidation state and coordination of Fe in biochars. Consistent with the XRD results, 79% of Fe in biochar produced from FeCl₃ treated cellulose was magnetite (Table S2). Iron in the 700 °C HTT Fe-biochar prepared from corn stover was mostly γ-Fe₂O₃ (73%) with lesser amounts of magnetite (10%) and an unidentified phase (13%). Iron in the 700 °C HTT Fe-alfalfa meal biochar was also primarily γ-Fe₂O₃ (52%) with smaller amounts of magnetite (20%) and Fe⁰ (28%). The decreased intensity of magnetite reflections in the XRD patterns of the Fe-corn stover and Fe-alfalfa biochars is consistent with the lower magnetite content in these biochars. Overall we observed a good fit of the model with the raw Mössbauer spectra (Fig. S2); however the fit was less satisfactory for the low-velocity doublet in the center of the spectra of 700 °C HTT Fe-cellulose and Fe-corn stover biochars. Recent work by Gabbasov et al. (2014) demonstrated that

the Mössbauer spectrum of γ -Fe₂O₃ changes with particle size, evolving from the typical sextet to a doublet of low isomer shift with decreasing particle size (<20 nm) [22]. This is the same region in our spectra that was inadequately represented by our model; hence we infer that the unidentified Fe phase in the cellulose (21%) and corn stover (10%) biochars is nanosized γ -Fe₂O₃.

3.5 FTIR Analysis

FTIR spectroscopy revealed an influence of pyrolysis temperature on the surface chemistry of biochar. Spectra of the 500 °C HTT biochars from all feedstocks consistently provided evidence of aryl moieties: minor phenolic OH stretching from 3100 to 3600 cm⁻¹, aromatic C-H stretching at 3050 cm⁻¹, arene C-C and C-heteroatom stretching from 1400 to 1800 cm⁻¹, and aromatic C-H bending in the fingerprint region (Figs. S3,S4). Absorbance in the region spanning 1000 to 1200 cm⁻¹ reflects alkyl C-O stretching indicative of ether and alcoholic functional groups present in these biochars. The broad carbonyl band centered approximately at 1700 cm⁻¹ is most prominent in spectra of biochar derived from cellulose, although it is present in all spectra indicating some aldehyde, ketone, and/or carboxylate surface character to these biochars.

Greater condensed aromatic character of C is observed in the 700 °C HTT biochars (Figs. 5, 6) than in the 500 °C HTT biochars as evidenced by weaker absorbance in the region spanning 1000 to 1800 cm⁻¹ due to increased polynucleation of aromatic C-C and C-heteroatom stretching. Consistent with greater C content (Table S1), spectra of these higher HTT biochars also exhibit lower aromatic C-H, hydroxyl, carbonyl, and alkyl C-O character; revealing less O containing functional groups and greater arene C character achieved with greater pyrolysis temperature [9,10]. All control 700 °C HTT biochars exhibit carbonyl multiplets ranging 1500 cm⁻¹ to 1800 cm⁻¹, a phenomenon due to Fermi resonance of conjugated carbonyls within a collective

molecular orbital structure [23-25]. These weak vibrations have been described as characteristic of quinone and semiquinone structures [26,27].

Change in biochar carbonyl character is observed in association with the metal treatments. Spectra in Figs. 6 and 7 show decreased carbonyl multiplet vibrations in 700 °C HTT Al-biochars and 700 °C HTT Fe-alfalfa biochar. The carbonyl vibrations are unchanged relative to controls in spectra of the 700 °C HTT Fe-cellulose and Fe-corn stover biochars and no change in carbonyl character is observed in comparing spectra of the 500 °C HTT control and Al, Fe-biochars. The loss of carbonyl multiplets in spectra of 700 °C HTT Al- and the Fe-alfalfa biochars relative to the spectra of the control biochars suggests that the carbonyl groups in these biochars are either (1) no longer conjugated in large molecular orbital systems or (2) that some carbonyls coordinated with the metals.

The alkyl C-O stretch typically manifests from 1000 to 1200 cm^{-1} in model compounds and is observed in spectra of 500 °C HTT biochars (Figs. S2,S3) to shift to higher energy for biochars produced from Al-treated corn stover and alfalfa as compared to controls. Spectra of biochars produced at 700 °C similarly exhibit increased absorbance in the 1100 to 1300 cm^{-1} region and decreased absorbance in the 950 to 1100 cm^{-1} region for Al-biochars relative to controls (Fig. 5); suggesting development of new and/or alteration of existing alkyl C-O character associated with the Al-treatments. These data suggest shorter C-O bond lengths that vibrate at higher energies than observed with model compounds. Increased absorbance is also observed in the 1400 to 1600 cm^{-1} region of spectra for the 700 °C HTT Al biochars relative to controls, suggesting that the Al treatment increased mobility of aromatic C and may have decreased the degree of polynucleation of arene C, probably by oxidation. Similar changes are observed in spectra of 700 °C HTT Fe-alfalfa meal biochar but not in spectra of Fe-cellulose or Fe-corn stover biochars

produced at the same temperature. Lack of increased absorbance in the 3100 to 3600 cm^{-1} region of spectra for metal biochars indicates alcohols likely did not form. Further, the thermal lability of carboxylates precludes their existence in 700 °C HTT biochars [27]. Thus, the altered alkyl C-O character observed with metal treatments is suggestive that O heterocycles were involved in the metal bonding.

$\gamma\text{-Al}_2\text{O}_3$ is the dominant crystalline form of Al_2O_3 heated above 500 °C [28]. Evidence of minor hydroxyl stretching in the 3000 to 3700 cm^{-1} region indicates some hydroxyl character to $\gamma\text{-Al}_2\text{O}_3$, likely due to adventitiously chemisorbed moisture that occurred with handling prior to FTIR analysis. The broad band in the fingerprint region of spectra of Al-treated biochars reflects IR absorption by Al-O bonds and is also present in the spectrum of $\gamma\text{-Al}_2\text{O}_3$. Spectra of 500 °C HTT Fe-biochars likewise show contribution of magnetite, the dominant mineral phase in these biochars, to their IR absorption behavior (Fig. S2). Magnetite exhibits some absorbance in the 1000 to 1800 cm^{-1} functional group region and more in the fingerprint region due to combined $\text{Fe}^{3+}\text{-O}$ and $\text{Fe}^{2+}\text{-O}$ dipole changes. Though both Al and Fe structures produced in biochar contribute to absorbance in FTIR spectra, lack of IR absorbance by $\gamma\text{-Al}_2\text{O}_3$ in the 1000 to 1300 cm^{-1} region in addition to increased absorbance in this same region observed in spectra of 700 °C HTT Al-biochars and the 700 °C HTT Fe alfalfa biochar clearly indicate that these metals reacted with biomass during pyrolysis, adding alkyl C-O surface character to the resulting biochar. Thus we infer the formation of alkyl C-O-Al and C-O-Fe structures on these metal treated biochars.

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Fi

278 g. 5: FTIR spectra of Al-biochars produced at the HTT of 700 °.

Fig. 6: FTIR spectra of Fe-biochars produced at the HTT of 700 °C.

3.6 XPS Analysis

Multi-component chemical models were employed to understand biochar surface chemistry and to assess the effects of the metal treatments and relationships between feedstock composition and pyrolysis temperature. C 1s spectra were deconvoluted to a four-component model which differentiates C bonded to C; singly bonded to O; doubly bonded to O, and inorganic carbonates (Fig. 7) [29]. O 1s spectra were deconvoluted to a three-component chemical model based on oxides and sp^3 O (alcohols / ethers); O_I , sp^2 O as found in carbonyls; O_{II} , and O associated with water (Fig. 7). N 1s spectra were deconvoluted to a two component model representative of 6

member N heterocycles, pyridinium groups, and 5 member N heterocycles, pyrroles and pyridones, as previously reported [9] (Fig. 8). These results are reported in Table S3.

C 1s spectra show differences in biochar surface chemistry related to feedstock and pyrolysis temperature. The low binding energy component centered at 284.6 eV is of greatest content for all biochars, indicating that C bonded to C comprises most of biochar surfaces. This component is greatest for biochar produced from cellulose and least for biochars produced from alfalfa. Accordingly, the C-O component centered at 285.9 eV reveals the opposite trend, suggesting that C singly bonded to O increases for biochars produced from cellulose < corn stover < alfalfa. The same trend is observed with the C=O component, however this component is likely not wholly represented by carbonyl C as C bonded to oxonium (287.3 eV) [9] is poorly resolved.

For biochars with complex elemental composition, electronegativity and electron donating effects must be considered which can shift the binding energies of classical functional groups [30]. Higher pyrolysis temperatures typically enrich C in biochars relative to O, H, and N and also increase the degree of polynucleation and arene character of organic C [30,31]. Consistent with reported data that demonstrate this phenomenon [30], C content of cellulose control biochars (Table S1) clearly show greater C content and FTIR data (Figs. 5,6) reveal greater arene C character with less O functionality in biochars produced at 700 °C versus 500 °C. However, C 1s XPS reveals decreased C-C and increased C-O components produced with increased pyrolysis temperature (Table S3), suggesting increased oxidation of biochar C with the increase in HTT. Peak maxima of the C-O and C=O components exhibit higher binding energies in biochar produced at 500 °C versus those produced at 700 °C. This phenomenon is likely due to differential charging of biochar samples whereby 500 °C samples exhibit greater charging and hence higher binding energies of C core shell electrons during photon excitement in contrast to

700 °C samples. This difference in surface charging behavior is due to differences in biochar electrical conductivity: biochars produced at 700 °C are more electrically conductive than those produced at 500 °C due to increased aromatic character, facilitating electrical grounding during XPS measurement [32].

We interpret the increased oxidation of biochar C observed with greater HTT not as increased C bonded to O, but as electron deficiency in the π aromatic C continuum caused by electronegative O containing functional groups which abstract electron density from the large molecular orbitals of condensed aromatic systems. Greater AEC and PZNC of the 700 °C biochar produced from cellulose at alkaline pH attests to greater positive surface charge and, hence, oxonium content produced at this pyrolysis temperature. Thus, charging behavior, aromaticity and electrical conductivity of C, and complementary data must be considered to understand the effects of biochar functional groups on XPS.

The metal treatments, particularly Al, demonstrated a strong oxidizing effect on organic O in biochar. Substantial Ca, K, and Si contents (Table S1) and XRD evidence (Figs. 3,4) for quartz in biochars produced from alfalfa and corn stover provide evidence for carbonates and oxides which confound the O_I component. Biochar produced from cellulose, however, has negligible ash [9], thus O observed in O 1s spectra of control biochars is, within the limits of measurement error, purely organic O. Though oxides and hydroxides of Al and Fe exhibit binding energies in the O_I region, the relatively low amounts of these metals on biochar surfaces (Table S4) indicate that observed O is dominantly organic. The metal treatments effected a transition of O_I surface character to O_{II}; less at 500 °C and more so at 700 °C, with more pronounced oxidation of O incurred by Al. Based on classical chemical models, this transition brought about by the metal treatments may be interpreted as conversion of organic O from alcoholic and ether to carbonyl,

335 however FTIR data demonstrate a shift in alkyl C-O stretching to higher energy and possible
336 deconjugation of carbonyls. Thus, the oxidation of organic O in biochar by Al and Fe is
337 consistent with oxidation of O associated with alkyl C-O bonds, causing O 1s electrons to have
338 higher binding energy than typically observed in model compounds. This change in the
339 chemical environment of O can only be effected by the abstraction of electron density likely
340 caused by bonding with cationic Al and Fe. Deconvolution of the Al 2*p* and Fe 2*p* regions
341 yielded single component models with binding energies that ranged from 74.4 to 76.0 eV for Al
342 2*p* and 711.3 to 712.2 eV for Fe 2*p*_{3/2}; indicating trivalency of both metals.

Figure 7: C 1s (**left**) and O 1s (**right**) XPS spectra of biochars derived from cellulose.

Nitrogen on biochar surfaces was incorporated in 5 and 6 member heterocycles (Fig. S5), consistent with previous reports [9,33,34]. Higher pyrolysis temperature caused a decrease in the relative amount of pyridinium type N and the metal treatments showed no effect on N content or type of surface N. Biochar produced from alfalfa contained more pyridinium type N than biochar produced from corn stover, illustrating the influence of feedstock biochemistry on resultant biochar surface chemistry. While pyridinium groups contributed to AEC at low pHs (pKa ~ 5.2), the low amounts of this surface structure observed by XPS (Tables S2,S3) illustrate that pyridinium moieties do not substantially contribute to biochar AEC.

3.7 Discussion

Pyrolysis of biomass pre-treated with Al or Fe trichlorides yielded various forms of these metals in the resulting biochars. Broad distributions of Al and Fe are observed, with greater dispersion resulting from covalent bonding between these metals and biochar surfaces. Iron presented a range of oxidation states in biochar, yielding Fe⁰, magnetite, and γ -Fe₂O₃ (Table S2); illustrating a range of reducing conditions during pyrolysis that is related to feedstock. XRD and SEM-EDS analyses demonstrate a heterogeneous distribution of Fe in biochar including large crystalline aggregates and dispersed Fe oxides, while Al was dominantly dispersed as amorphous oxide phases. Despite internal structure of metal phases, their external surfaces are oxides as shown by SEM-EDS and XPS analyses (Figs. 1,2). The distribution and mineralogy of Al and Fe strongly influence biochar surface chemistry and resulting AEC.

Multiple mechanisms contribute to biochar AEC. The pH-dependent AEC in control biochars is attributed to protonated pyridinium moieties and basal planes of condensed aromatic C,

whereas pH-independent AEC is attributed to oxonium heterocycles [9]. Metal oxyhydroxides form by hydration and subsequent reaction of metal oxides with water and thus formed on the Al and Fe oxide phases produced in biochars derived by the metal treatments. In accordance with Pauling's Rules [35], strength of the bond between the metal and oxygen, hydroxide, or water molecule in a coordination polyhedron is determined by the valence of the metal cation divided by the coordination number. For octahedrally coordinated trivalent Al and Fe with six ligands, the formal charge on exposed non-bridging OH groups would be $-1/2$ while H_2O groups will carry a formal $+1/2$ charge. At pHs below PZNC, Fe and Al oxyhydroxides become increasingly protonated, accruing positive charge [36], thereby exhibiting pH-dependent AEC. The coordination number of Al and Fe covalently bonded to biochar surfaces and the relative ionic character of metal-OH/ H_2O bonds are likely to vary depending on the local chemical environment, which will influence the PZNC and AEC.

These oxyhydroxide surface features exhibit mixed effects on total biochar AEC and PZNC. The effect of biochar surface enhancement by metal oxyhydroxides on AEC depends on the distributions of these structures over the external surfaces of biochar and their PZNCs. Contributions from these structures only partly account for total AEC and are highly pH-dependent. Different crystalline phases formed from metals, exhibiting different PZNCs which influence AEC. Evidence for magnetite and maghemite in 700 °C HTT biochars produced by the Fe-treatment indicate that the different Fe mineralogies can influence AEC as magnetite has PZNC as low as pH 3.8 and both magnetite and maghemite exhibit broad ranges of PZNC [12]. At pH 8, the effect of oxyhydroxides is well pronounced with increases in AEC being observed by both metal treatments in biochar derived from alfalfa meal and cellulose (Table 1). At this pH, Fe and Al oxyhydroxides are only partly positively charged based on our PZNC data,

however these metals are more abundant than oxonium heterocycles in some biochars and, thus, increased AEC relative to the control. Biochar derived from corn stover exhibited greatest oxonium heterocycle content among all biochars [9] and the effect of metal oxyhydroxides did not significantly outweigh this source of AEC. Greater metal loading during biomass pretreatment may have yielded different results, however the data show that at pH 8, oxyhydroxides can contribute more to total AEC than mechanisms attributed to the C fraction of biochar; meriting further research in optimizing metal content and feedstock selection to maximize AEC.

Under acidic pHs, AEC endogenous to biochar C can account for a larger fraction of total AEC than that contributed by oxyhydroxides. This effect is largely influenced by the distribution of metals on the surface of biochar. All biochars exhibit increased AEC with decreased pH. Oxyhydroxides acquire greater positive surface charge as pH decreases and this can influence total AEC depending on the distribution and nature of the oxyhydroxide phases on the biochar surfaces. The Al treatment generally increased AEC in all biochars at acidic pHs, although these changes were not always significant. However, the Fe treatment yielded the opposite effect, actually decreasing AEC or exhibiting no significant effect at acidic pH, likely due to the low PZNC contributed by magnetite on biochar surfaces.

Iron was more dispersed on surfaces of biochar derived from alfalfa meal than from cellulose, (Figs. 2,S1) yet the net effect of this treatment was to lower AEC versus the control or exhibit no significant change. Aluminum was well dispersed on the surface of biochar derived from cellulose and likewise caused AEC to increase in this biochar. The metal phases occlude the carbonaceous surfaces of biochar potentially masking or displacing oxonium groups which otherwise would contribute to AEC. Thus, metal oxyhydroxides can increase or decrease AEC

in biochar, depending on the distribution of these phases and the resulting positive charge density these surface enhancements can impart to biochar.

Dispersion of metals on biochar surfaces is key to efficient use of pre-treatment materials and in creating oxyhydroxide surface coatings. The distribution of metals in biochar was influenced by their coordination with O functional groups in biomass during pyrolysis. FTIR spectral evidence demonstrates transformation of alkyl C-O character to shorter C-O bond lengths in biochar produced at both HTTs employed in this study (Figs. 6,7,S3,S4). Consistent with this observation, XPS revealed oxidation of biochar O incurred by the metal treatments, especially by Al, at 700 °C HTT. While the chemical environment of C was not affected by the metal treatments, the presence of trivalent Al and Fe and oxidation of O revealed by XPS and the lack of evidence for increased carbonyl character indicate that these metal cations had coordinated with *sp*³ O heterocycles in biochar, resulting in C-O-metal surface features. We suggest that the C-O bond length of this bonding structure is shorter than that of typical alkyl C-O bonds. This bonding was particularly observed with Al and led to its dispersion across biochar surfaces as observed in the SEM-EDS analysis of biochar produced from cellulose (Fig. 1). While some oxidation of biochar O was observed with the Fe treatment, Fe did not efficiently bond to biochar surfaces, resulting in aggregation of Fe and formation of detectable crystalline phases. Formation of C-O-metal bonding structures in biochar has not been previously reported in the literature and has implications for the development of carbon-supported metal oxides for various applications: heterogeneous catalysts, bio-renewable ion exchange media, and other functionalized biochars tailored for specific applications.

The scope of this study is limited to investigating the production of, and surface chemistry of, metal treated biochars. In the future, various industrial and environmental applications for high AEC metal-treated biochars, such as the removal of oxyanions and organic acids from potable and effluent water, may be developed, however much additional research is needed first. Ultimately, disposal of spent biochar from various applications and biochar deployed for environmental use would sequester atmospheric C in soil and biochar that contain metals such as Al and Fe will not adversely impact environmental quality as these earth abundant metals are found in clay minerals and sesquioxides, thus the environmental fate of biochar produced with these metals would likely enter well-understood biogeochemical cycles with the oxidation and hydrolysis of organometallics formed during pyrolysis.

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Competing Financial Interests

The authors declare no competing financial interests.

Additional information

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