Biochar for sustainable advances in agriculture and environmental remediation

Michael Lawrinenko
Iowa State University

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Biochar for sustainable advances in agriculture and environmental remediation

by

Michael Lawrinenko

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Majors: Soil Science (Soil Chemistry) and Environmental Science

Program of Study Committee:
David Alan Laird, Co-Major Professor
Johannes van Leeuwen, Co-Major Professor
Robert Horton
Michael Thompson
Gordon Miller

Iowa State University
Ames, Iowa
2016

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I dedicate this dissertation to God who has given me the intellect and other abilities necessary to successfully conduct and present the research reported herein. Also, to my children Ilaria, Emilia, Anthony, Zhenya, and Mykola, (and hopeful future offspring!!), and my wife Ludmyla who have persevered with me through these difficult years; and to Olga who has a deep appreciate for the environment and green living. By God’s grace, may the talents I have developed in my training and the contributions I have made and continue to make to science benefit mankind and all posterity through improvements in sustainable agriculture and advancements in environmental remediation.
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ABSTRACT

Biochar is the solid residue of organic materials heated under low-oxygen conditions and is a co-product of pyrolysis based bioenergy production (PBBP) in which biorenewable materials are utilized to produce energy. Biochar exhibits long residence times in soil, thus soil application can sequester atmospheric carbon. Biochar can also improve soil properties. Biochar can contribute to the success of PBBP by high economic value, however, variable properties and performance in soil preclude agronomic recommendations, limiting application and hence, demand and value. Biochar with significant anion exchange capacity (AEC) has potential to become a co-product of PBBP with implications for sustainable agriculture and environmental remediation, however knowledge of the persistence of biochar AEC and the mechanisms by which biochar surface chemistry changes as it ages and weathers in soil environments was lacking. This research intended to investigate biochar ageing, ageing impacts on AEC, increase AEC for alkaline pHs, and produce biochar for the remediation of chlorinated hydrocarbon contaminants (CHCs). Biochars were oxidized under alkaline conditions to understand ageing in relevant conditions and enhanced with metal oxyhydroxides to increase AEC. Pyrolysis temperature influences aromatization of biochar carbon which oxidizes by pathways related to degree of aromatization and exhibits ageing recalcitrant AEC due to position stabilized oxonium heterocycles. Metals can form organometallic bonding structures in pyrolysis that can increase biochar AEC by the high points of zero net charge (PZNC) of metal oxyhydroxides. Pyrolysis can be used to reduce iron to yield biochar-zerovalent iron (BC-ZVI) which can reductively dechlorinate CHCs. Feedstocks low in silicon and phosphorus yield BC-ZVI suitable for this purpose. High AEC biochar and
BC-ZVI add value to biochar, increasing the economic competitiveness of PBBP, and proffer green advances to existing production technologies.
CHAPTER 1. INTRODUCTION

Biochar is an important co-product in pyrolysis based bioenergy production (PBBP). Biochar is the solid residue of biomass heated under low-oxygen conditions and was proposed as a means to sequester atmospheric carbon by converting plant assimilated carbon dioxide to a stable, solid form and apply it to soil.\textsuperscript{1,2} Studies concerning the Terra Preta soils of the Amazon Basin revealed that anthropogenic additions of charcoal improved soil fertility and crop production.\textsuperscript{3} Studies of the fertile Iowa Mollisols have likewise revealed that charcoal carbon constitutes a significant fraction of soil organic matter.\textsuperscript{4,5} Hence, biochar-soil interactions have sparked a significant research interest culminating in thousands of peer-reviewed research papers published since the concept of applying biochar to soil was proposed.\textsuperscript{6} However, broad variability of biochar properties\textsuperscript{7} has led to equally variable results reported in many biochar-soil studies,\textsuperscript{8-10} making it difficult to make agronomic recommendations for biochar applications. Biochar has also been investigated as a means to more sustainably produce catalysts,\textsuperscript{11} activated carbon,\textsuperscript{12} novel magnetic adsorbents,\textsuperscript{13} phosphate trap for soil remediation,\textsuperscript{14} and hydrogen storage\textsuperscript{15} using biorenewable materials. These green advents in technology can increase the profitability of pyrolysis based bioenergy and promote economic growth in rural communities while providing sustainable alternatives to meet consumer needs.

Physical and chemical properties of biochar vary with feedstock properties and production conditions.\textsuperscript{9,16} This presents challenge and opportunity to the growing biochar industry and PBBP. As with any product, consistent properties and reliable performance are critical to consumers and the success of biochar producers. The challenge to produce biochars with consistent and reliable properties requires understanding the effects of
production conditions and feedstock properties on the properties of biochar. Hence, it is imperative to understand the relationships between feedstock composition and structural chemistry and those of biochar, the thermochemical transformations that occur during pyrolysis, and the influences of process variables, such as heating temperature, on the structural and surface chemistry of biochar.

Understanding service life and persistence of properties is critical to the success of any product. Therefore, it is also important to understand how biochar changes in environments of application. For example, biochar in soil environments have been demonstrated to oxidize and exhibit changes in surface chemistry, however the mechanisms by which biochar oxidizes are poorly understood. Thus, one goal of this dissertation was to understand biochar oxidation, particularly oxidation of biochar in alkaline environments characteristic of many Mollisols, which produce most of the legume and cereal crops in the world and dominate the landscape of Iowa.

Economics challenge the success of PBBP and hence biochar production. Biorenewable energy production must compete with the cost of petroleum and other fossil fuels. High values of biochar can increase the competitiveness of PBBP, however biochar must offer more than carbon sequestration, but also offer other advantages to soil or have other, high value applications as some studies have reported. Widespread PBBP as described in the Charcoal Vision could potentially generate vast amounts of biochar which may exceed the needs for niche applications, saturating the market and lowering the value of biochar. The need to improve nutrient use efficiency and to reduce the harmful environmental consequences of nutrient leaching of nitrate and phosphate from agricultural soils could create a large demand for biochar.
Biochars with anion exchange capacity (AEC) could adsorb nitrate and phosphate. When applied to soil, biochars with significant AEC could thus help retain these nutrients in the soil where plants need them. An integrated PBBP system which produces high AEC biochars that would help retain nitrate and phosphate in the soil could proffer increased sustainability to modern agriculture through increased nitrogen and phosphorus use efficiency and improved environmental quality, with carbon sequestration as an ancillary benefit. Other interventions to improve environmental quality could also be explored with the availability of low-cost and abundant anion adsorbent. Adsorption of heavy-metal oxyanions, virulent Gram positive organisms from municipal effluents, and organic acids which can plague potable water production are just a few possible applications in which biochar with significant AEC could be used; all contributing to the demand for high AEC biochars.

Biochars can be produced with significant AEC, however there was a lack of understanding of how biochar AEC changes as it weathers and ages in the soil. The persistence of biochar AEC was also poorly understood, making it difficult to make agronomic or geoengineering recommendations for the application of biochars based on their ability to adsorb anions. A systematic approach was therefore employed to understand the influences of feedstock composition and pyrolysis temperature on biochar surface chemistry, mechanisms of oxidation, and the impact of oxidation on biochar anion exchange capacity (AEC). This knowledge could facilitate making appropriate recommendations for the production and application of biochars with significant AEC for soil use, enabling PBBP with a co-product that could be applied to soil, thus creating widespread demand for and added value to biochar.
There exist many potential applications for biochar with significant AEC. However, AEC is a dynamic property that changes with pH of soil and water. Biochar AEC is contributed to by several mechanisms: 1) the protonation of basic sites such as nitrogen heterocycles, 2) protonation of aromatic carbon rings which can stabilize proton, and 3) oxonium heterocycles\textsuperscript{16}. The first two mechanisms are highly pH dependent, contributing to AEC under acidic conditions. In contrast, oxonium heterocycles contribute to pH-independent positive surface charge. Though this latter mechanism of AEC contributes to anion adsorption at any pH, oxonium character to biochar surfaces is limited, hence biochar AEC under alkaline conditions is likewise limited; rendering biochar intended for anion adsorption ineffective when applied to alkaline soils or used in other alkaline applications.

This limitation of biochar AEC also limits its applicability and need. Thus, another goal of this dissertation was to augment biochar AEC, particularly at higher pHs. It was hypothesized that metal-oxyhydroxide surface enhancement could increase biochar AEC and that organometallic bonding structures could be created in pyrolysis that would bond metals to biochar surfaces. Aluminum and ferric chloride salts were selected to pretreat biomass as these earth-abundant metals inherently compose soil 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 in pyrolysis.

Of the many contaminants that threaten environmental and human health, chlorinated hydrocarbons such as trichloroethylene (TCE) are particularly endangering due to their environmental persistence and toxicity.\textsuperscript{20} With 427 superfund sites in the United States having groundwater contaminated with TCE,\textsuperscript{21} this contaminant has become a widespread
problem. An effective remediation strategy is reductive dechlorination by reduced metals such as zerovalent iron (ZVI) emplaced in soil as permeable reactive barriers (PRBs).

There exists a need for low-cost and effective materials for the remediation of TCE because ZVI is costly at prices exceeding $800 per ton (personal communication with Hepure, Concord, CA). Moreover, current ZVI production methods carry a significant climate impact associated with coal fired reduction of iron. Recent reports of ZVI production in pyrolysis demonstrated that biomass pretreated with iron salts can be pyrolyzed yielding biochar-zerovalent (BC-ZVI) composites and that TCE is more rapidly degraded by ZVI compositing with adsorbents such as biochar and activated carbon than by ZVI alone. However, understanding the transformations of iron during pyrolysis and the influences of feedstock chemistry and heating temperature on ZVI production was lacking. Hence, another goal of this dissertation was to understand these transformations and to present a greener and more sustainable pathway to produce low-cost ZVI for environmental use. Lastly, BC-ZVI was synthesized using lignin and magnetite to present a method to produce macroporous BC-ZVI from a biorenewable, industrial waste residual and a common iron oxide to develop macroporous carbon supported ZVI for use as PRB media. Transport and degradation of aqueous TCE through granular BC-ZVI was studied in a column experiment using a convection-dispersion chemical transport model to evaluate this material for use as a PRB. These studies contribute to science and proffer more sustainable and greener advances to technologies pertinent to the remediation of contaminated soil and groundwater.

References


CHAPTER 2.

ACCELERATED AGING OF BIOCHARS; IMPACT ON ANION EXCHANGE CAPACITY

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Michael Lawrinenko,a David A. Laird,a*, Robert L. Johnson,b and Dapeng Jingc

*a* Corresponding author: David A. Laird  
a Department of Agronomy, Iowa State University, Ames, IA, USA, 50010  
b Department of Chemistry, Iowa State University, Ames, IA, USA, 50010  
c Materials Analysis and Research Laboratory, Iowa State University, Ames, IA, USA, 50010

Abstract

Little is known about the stability of biochar anion exchange capacity (AEC) and by what mechanisms AEC changes as biochar ages and weathers in soil environments. The goal of this study was to investigate chemical changes that may occur during ageing of biochar in neutral or alkaline soils and to assess the impact of ageing on AEC. To simulate and accelerate ageing, biochars were oxidized in alkaline hydrogen peroxide for 4 months. Spectroscopic evidence (*FTIR, XPS and 13C-NMR*) revealed that ageing increased carbonyl and alcoholic character in biochars produced at 500 °C and effected endoperoxide formation in biochars produced at 700 °C; the latter exhibited greater arene carbon character. Ageing caused biochar AEC to decline on average by 54% with greater decreases in biochars produced at 500 °C in contrast to biochars produced at 700 °C. The AEC of biochar derived from alfalfa meal and cellulose produced at 700 °C did not change significantly (p = 0.20 and p = 0.50, respectively) with ageing. Stability of AEC in the high temperature biochars is attributed to the presence of oxonium groups in bridging positions of arene carbon, which are sterically resistant to nucleophilic attack.
2.1 Introduction

Biochar is the solid residue obtained from the pyrolysis of biomaterials. Anion exchange capacity (AEC) is a little studied but critically important property of biochar that will influence its value. Soils amended with high AEC biochar may exhibit reduced nutrient leaching. Furthermore, biochars with high AEC have the potential to be used in water treatment for the removal of anionic contaminants; hence high AEC is a potentially useful property that may contribute to biochar value. In previous work, we demonstrated that biochars can be produced with considerable AEC. Measured AEC values ranged from 0.602 to 27.76 cmol Kg$^{-1}$ for biochars produced from alfalfa meal, cellulose, and maize stover. We identified oxonium groups, pyridinium groups, and the adsorption of protons by the basal planes of π ring systems in condensed aromatic C as likely sources of the positive charge responsible for AEC. [1] Understanding the stability of biochar AEC in various environments is important as AEC stability will have a large influence on potential product use and hence value.

The surface chemistry and various physical and chemical properties of biochar are known to change with time in soil environments. However, there has been only one prior study that has addressed the stability of AEC in biochar. Cheng et al. [2] measured moderate AECs of 9.92 and 6.96 cmol Kg$^{-1}$ for biochars produced from oak using traditional kiln methods. After incubation for 12 months at 30 °C, AEC declined to 1.80 cmol Kg$^{-1}$, and biochar incubated for 12 months at 70 °C exhibited negligible AEC. Biochar coated with humic acid exhibited an AEC of 5.8 cmol Kg$^{-1}$, a slight decrease from the fresh biochar AEC of 8.4 cmol Kg$^{-1}$. This decline in AEC was attributed to surface
conditioning with humic acid, not the degradation of AEC functional sites. The evidence presented by Cheng et al. [2] indicates that biochar AEC decreases with exposure to soil environments, yet the mechanisms responsible for change in AEC are not understood.

Anion exchange sites in biochar may change due to oxidation. Oxidation of biochar results in an increase in O containing functional groups; specifically hydroxyl, carboxylate, and aldehyde moieties [2,3]. Cheng et al. [2] reported Fourier transform infra-red (FTIR) spectroscopic evidence of significant increase in hydroxyl and carbonyl character of biochars recovered from 130 year old kiln sites and biochars incubated for 12 months relative to freshly made biochars prepared by similar methods. Elemental analysis confirmed an increase in O content in the kiln site and incubated biochars. Though not discussed in their publication, an increase in absorption in the 1100 to 1300 cm\(^{-1}\) range in Fig. 2 is consistent with alkyl C-O stretching, suggesting that these bonding structures are also generated during oxidation of biochar. They reported an increase in negative surface charge and a decrease in isoelectric point of the aged biochars; due to carboxylation of biochar surfaces with ageing. Formation of carboxylate groups on biochar surfaces increases negative surface charge and cation exchange capacity (CEC) but does not contribute to biochar AEC.

Oxidation of biochar C by various oxidizing agents yields surface changes unique to the oxidant [4,5]. For example, Moreno-Castilla et al. [5] found that oxidation of activated carbon with nitric acid yielded nitro groups on the surface of the activated carbon while oxidation with hydrogen peroxide and ammonium persulfate treatments yielded more carbonyl and carboxylate moieties. Oxidation with hydrogen peroxide, in particular, generated more ether groups on the activated carbon surfaces. Biochars produced by
traditional kiln methods and incubated biotically developed carboxylate, lactone, and phenolic surface groups, with an increase in carboxylate character being the most prominent change [6]. Furthermore, different phase-dependent oxidation mechanisms may occur with carbon blacks, with formation of anhydride, carboxylate, and hydroxyl groups occurring in liquid phase treatments and carbonyl groups forming on the surfaces during vapour phase treatments [7].

Ageing of biochar in soil environments may be caused by a variety of mechanisms, including radical addition [8,9], reaction with superoxide anions [10], and reaction with singlet oxygen [11]. Biotic oxidation may involve hydrogen peroxide released by soil biota [12,13]. Oxidation of polyaromatic hydrocarbons and other organic compounds in aquatic environments by reaction with singlet oxygen (\(1^1\text{O}_2\)) has been demonstrated [14,15]. The fact that \(1^1\text{O}_2\) oxidizes dissolved organic compounds demonstrates that it is sufficiently stable in water to react in solution. \(1^1\text{O}_2\) is generated by photoexcitation of ground state oxygen in the air that may then diffuse into solution. Likewise, biochar at the soil surface is prone to reaction with \(1^1\text{O}_2\), with increased oxidation brought about by tillage events. In the soil, reactions with peroxides, \(1^1\text{O}_2\), and free radicals can occur depending on the chemistry of the biochar surfaces and the reductive-oxidative and pH conditions prevailing in the soil. Temperature, solar intensity, and soil moisture content all may influence reaction kinetics and mechanisms. Condensed aromatic carbon oxidizes slowly when exposed to reactive forms of oxygen; by contrast plant materials and microbial biomass in various stages of decomposition are much more rapidly oxidized. Ultimately, biochar does change with ageing [1,3] and we seek to understand the mechanisms by which ageing occurs and the impact of these changes on biochar AEC.
The purpose of this study was to characterize biochar reactions with $^{1}$O$_2$ under alkaline conditions in an effort to understand oxidation and other aging mechanisms that may occur in neutral or alkaline soil environments. To accelerate the ageing process, biochars were exposed to $^{1}$O$_2$ generated by Fenton transformed H$_2$O$_2$ in an alkaline environment. The impact of this ageing treatment on surface chemistry and AEC is assessed and reaction mechanisms are discussed.

2.2 Experimental

2.2.1 Biochar preparation

Biochars were produced from alfalfa meal, maize stover, and cellulose by slow pyrolysis using a muffle furnace at highest treatment temperatures (HTTs) of 500 °C and 700 °C. Details of biochar preparation are described in Lawrinenko and Laird [1]. Here fresh biochars refers to samples that were dialyzed against deionized (DI) water using Spectra / POR® MW 6-8000, 32 mm tubing until the electrical conductivity of the bath solution was stabilized. Oxidized biochars are subsamples (20 g) of the fresh biochars that were transferred to 125 mL high density polyethylene bottles and combined with 50 mL 1 M NaOH. Weekly, 1 mL of 30% H$_2$O$_2$ was added to this mixture, allowed to stand for 10 minutes, capped, and then shaken on a reciprocating shaker. This treatment was continued for a total of 4 months. pH of biochar slurries was checked using pH paper to ensure a high level of alkalinity throughout the oxidation treatment. On termination of this alkaline-oxidation treatment, biochars were rinsed with deionized water on 0.45 μm Teflon filter paper until conductivity of the rinsate was below 5 μScm$^{-1}$. The biochars were subsequently dried in a convection oven at 105 °C for 3 three weeks.
2.2.2 Elemental analysis

Fresh and oxidized biochar samples were analyzed in duplicate to determine C, N, H, and S content using an Elementar Vario Micro Cube combustion analyzer with argon as a carrier gas. Oxygen content was computed as the difference between the sum of C, N, H, and S mass fractions and unity for biochars produced from cellulose. The other biochars contained significant levels of ash which precludes accurate determination of structural O by difference.

A Philips PW 2404 X-ray fluorescence (XRF) spectrometer was used for bulk chemical analysis. The spectrometer was equipped with a rhodium X-ray tube that was operated at 3600 Watts for this analysis. The spectrometer was flushed with helium (He) gas during all measurements. All measurements were corrected for tube drift by monitoring a reference sample (AUSMON-silicate minerals reference monitor). For the analysis, 5 to 10 g biochar samples were ground in a SPEX shatterbox puck mill for two minutes and two gram subsamples were placed into disposable sample cups and sealed with polypropylene film (6-μm thick). Only single-sample measurements were made by XRF. No standard reference materials (SRMs) for the elements of interest were available with a comparable matrix. Therefore calibration standards were prepared by mixing the 700 °C cellulose biochar (0.92% ash) and the 700 °C alfalfa meal biochar (30.89% ash) with known quantities of reference standards, specifically NIST 1633a, NIST 2691, ACS Grade potassium chloride, USGS Nod-A-1, NIST 2910, and AWP Std I.
2.2.3 FTIR Analysis

FTIR spectra of biochar samples were obtained using a Nicolet 560 Magna - IR spectrophotometer using the diffuse reflectance accessory. Absorbance spectra were recorded from 4000 to 400 \( cm^{-1} \) at a resolution of 4 \( cm^{-1} \). A total of 200 scans were averaged to produce the final spectra. Biochars were co-ground with spectroscopy grade KBr in a SPEX 5100 mixer mill at 1% wt/wt in KBr. Spectra were interpreted using published tables [16].

2.2.4 \(^{13}\)C solid state NMR spectroscopy analysis

\(^{13}\)C nuclear magnetic resonance (NMR) spectroscopic analysis was performed on biochars derived from cellulose. Two methods were employed due to the lack of \(^1\)H present in the 700 °C material, and the short T1C. Spectra of 500 °C HTT biochars were acquired using Multi-CP, a recently developed quantitative cross polarization (CP) technique [17] at 100 MHz using a Bruker DSX400 spectrometer and a Bruker 4-mm \(^1\)H–\(^{13}\)C double-resonance magic angle spinning (MAS) probe head at 14 KHz. Biochar samples were ground in a SPEX shatterbox puck mill for two minutes and were packed into 4-mm diameter zirconia rotors with 5-mm long glass inserts at the bottom to constrain the samples to the space within the radio frequency coil. The Multi-CP experiments used a \(^1\)H repolarization delay of 0.5 s with a ten-step \(^1\)H ramp of 90-100% of optimized CP conditions. Each CP period was looped six times totaling 50 ms of cross-polarization followed by a 1 s recycle delay. A 4\(\mu s\) \(^1\)H and 4.5\(\mu s\) \(^{13}\)C 90° pulse lengths were used with 60 kHz \(^1\)H decoupling during acquisition and during the Hahn echo.
Carbon moieties were assayed relative to total carbon based on cumulative NMR response in the following regions: carbonyl C 164 – 200 ppm, aromatic C 90 – 164 ppm, ether or ester (o-alkyl) C 61 – 90 ppm, and alkyl C 0 – 61 ppm. Aromatic C not bound to O (90 – 143 ppm) was differentiated from aromatic C bound to O (143 – 164 ppm) with assignment of aromatic C two bond lengths from O in the range of 90 – 120 ppm and aromatic C greater than two bond lengths from O in the range of 120 – 143 ppm. Individual regions in the spectra were integrated from boundary to boundary. Region total area fractions were determined and are reported as fraction of C type.

The 700 °C HTT biochars were analyzed by solid state direct polarization (DP) NMR using an Avance II 600 NMR spectrometer, featuring a wide bore 14.1 T superconducting magnet. Biochar samples were ground in a SPEX shatterbox puck mill for two minutes then packed into 2.5 mm solid-state NMR rotors, with approximately 7.5 mg of biochar packed in each rotor. The $^{13}$C spectra were obtained using a $^{13}$C single pulse sequence with high powered $^1$H decoupling, under 24 kHz magic angle spinning. The sequence used a 5 $\mu$s $^{13}$C 90° pulse followed by an acquisition time of 13.5 ms under 100 kHz $^1$H TPPM decoupling. Each spectrum was averaged over 16384 scans with a 5 second recycle delay, calibrated to ensure full signal relaxation time in between each scan. The spectral width was 75 kHz, or 500 ppm, centered at 115 ppm.

2.2.4 XPS analysis

Spectral measurements were performed using a Kratos Amicus/ESCA 3400 instrument, using unmonochromated Mg $K\alpha$ x-rays generated at 240 W.
Photoelectrons emitted at 0° from the surface normal were energy analyzed using a DuPont type detector. The pass energy was set at 75 eV and a Shirley baseline was removed from all reported spectra. Deconvolution of C1s spectra was performed using Casa XPS.

### 2.2.5 AEC analysis

Anion exchange capacity was measured in triplicate using bromide as the index anion and chloride as the replacing anion. Biochar samples (1g, accurately weighed) in Milli-Q water were equilibrated to pH 6 by adding HBr, saturated with Br by adding 1M KBr, rinsed to remove excess salt, and the retained Br⁻ was displaced by washing with 2.5 M CaCl₂. The solution containing the extracted Br⁻ was diluted to a known volume and a subsample was analyzed for Br⁻ 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. A complete description of the AEC method is given in Lawrinenko and Laird [1].

### 2.2.6 Statistical analysis

Statistical analysis of AEC measurements was performed using SAS 9.3 (GLIMMIX, SAS 9.3, SAS Institute Inc., Cary, NC, USA). Data was treated using a 2-way ANOVA in a randomized complete block design in which individual biochars were treated as blocks. The fixed effect of age, fresh versus oxidized biochars, was assessed as well as the block effect and the 2-way interaction.
Unpaired t-tests for differences between AEC means of fresh versus oxidized biochars were also performed and reported at the 0.05 significance level.

2.3 Results

2.3.1 Compositional changes

Oxygen is a component of many polar functional groups that accrue with oxidation and therefore the structural O content of biochars is an important indicator of the extent of biochar oxidation. Quantifying structural O in biochars, however, is difficult because O is associated with both organic and inorganic phases. Inorganic phases such as oxides, hydroxides, and carbonates are formed both during pyrolysis when biochar is produced and during the combustion of biochars. The thermal lability of carbonates, hydroxides, and hydrates alludes that the stoichiometry of inorganic mineral phases can change during combustion, which is central to analysis of C, N, and H by combustion analysis techniques. Hence, determining structural O by subtracting ash, C and H from unity is not accurate for biochars that contain significant amounts of ash. Acid washing biochars will remove accessible salts, carbonates and hydroxides but will not remove all mineral phases and can effect changes in surface chemistry and structural O composition. Thus the structural O content of acid washed biochars determined by difference may not accurately reflect the structural O content of the original biochar. For these reasons, we determined structural O content by difference from unity after subtracting the C and H fractions only for the cellulose biochars as the cellulose used in this study had negligible ash content and therefore was not subject to the above discussed errors.

Carbon content decreased among all biochars following the ageing treatments (Table 2.1), as would be expected assuming an increase in O content with oxidation. The 500 °C
and 700 °C cellulose biochars accrued 2.7% and 8.4% O, respectively, during ageing. The greater increase in O content of the 700 °C cellulose biochar suggests a different reaction pathway for the 700 °C biochar in contrast to the 500 °C biochar. Nitrogen content of the alfalfa meal biochars did not change appreciably following the ageing treatments, while a large decrease in N after these treatments was observed for the maize stover biochars. Nitrogen content of the original cellulose and the cellulose biochars was negligible. Ageing decreased H content in all but the 700 °C HTT cellulose and maize stover biochars. The slight increase in H content of the 700 °C cellulose and maize stover biochars following ageing may be due to abstraction of H from H₂O by radicals formed during pyrolysis and by basal planes of condensed aromatic C, which act as strong Lewis bases [9,18,19]. The S content of the biochars decreased following ageing (Table 2.1), indicating that S functional groups are labile under alkaline and oxidative conditions. Changes in composition of the 700 °C HTT alfalfa meal biochar due to ageing were minor and the H content of this biochar was lowest among biochars in this study suggesting that the 700 °C alfalfa biochar may have had a greater degree of condensation of aromatic C in contrast to the other biochars which promoted stability.
Table 2.1  C, N, H, S, and O contents of fresh and aged biochars.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>HTT (°C)</th>
<th>Age</th>
<th>% C</th>
<th>% N</th>
<th>% H</th>
<th>% S</th>
<th>% O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa</td>
<td>500</td>
<td>Fresh</td>
<td>66.03</td>
<td>3.40</td>
<td>2.43</td>
<td>0.18</td>
<td>*</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>700</td>
<td>Fresh</td>
<td>68.80</td>
<td>3.23</td>
<td>1.45</td>
<td>0.25</td>
<td>*</td>
</tr>
<tr>
<td>Cellulose</td>
<td>500</td>
<td>Fresh</td>
<td>84.80</td>
<td>0.00</td>
<td>2.98</td>
<td>0.08</td>
<td>10.82</td>
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<td>Cellulose</td>
<td>700</td>
<td>Fresh</td>
<td>90.30</td>
<td>0.01</td>
<td>1.72</td>
<td>0.12</td>
<td>6.12</td>
</tr>
<tr>
<td>Maize Stover</td>
<td>500</td>
<td>Fresh</td>
<td>75.45</td>
<td>1.48</td>
<td>2.67</td>
<td>0.08</td>
<td>*</td>
</tr>
<tr>
<td>Maize Stover</td>
<td>700</td>
<td>Fresh</td>
<td>77.54</td>
<td>1.23</td>
<td>1.48</td>
<td>0.13</td>
<td>*</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>500</td>
<td>Aged</td>
<td>61.46</td>
<td>3.57</td>
<td>2.18</td>
<td>0.11</td>
<td>*</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>700</td>
<td>Aged</td>
<td>68.01</td>
<td>3.39</td>
<td>1.22</td>
<td>0.15</td>
<td>*</td>
</tr>
<tr>
<td>Cellulose</td>
<td>500</td>
<td>Aged</td>
<td>83.68</td>
<td>0.00</td>
<td>2.76</td>
<td>0.02</td>
<td>13.54</td>
</tr>
<tr>
<td>Cellulose</td>
<td>700</td>
<td>Aged</td>
<td>81.83</td>
<td>0.01</td>
<td>3.56</td>
<td>0.07</td>
<td>14.53</td>
</tr>
<tr>
<td>Maize Stover</td>
<td>500</td>
<td>Aged</td>
<td>74.85</td>
<td>0.74</td>
<td>1.97</td>
<td>0.05</td>
<td>*</td>
</tr>
<tr>
<td>Maize Stover</td>
<td>700</td>
<td>Aged</td>
<td>71.25</td>
<td>0.00</td>
<td>1.62</td>
<td>0.10</td>
<td>*</td>
</tr>
</tbody>
</table>

Results are averages for duplicate analysis of samples. RSDs for C, N, H, and S in standards range from 1.3 to 3.2%. RSDs for C in biochar samples were <3%, while RSDs for N, H, and S in biochar samples were as high as 30% as concentrations of these elements approached the instrument detection limit. * not determined.

The alfalfa meal and maize stover biochars contained higher levels of inorganic elements than the cellulose biochar (Table 2.2). Nutrients, including P, Na, K, Mg, Ca, Si, Fe, Mn, and Zn, are present in plant tissue and are conservatively partitioned into biochars during pyrolysis due to their low volatility [20,21,22]. Other elements including Cr, Ti, and much of the Fe detected in the biochars probably leached from the stainless steel containment vessel during pyrolysis. The observed Cr (180 ppm) in the 700 °C cellulose biochar indicates the necessity of using the right materials in the construction of pyrolyzers to avoid heavy metal contamination of biochars intended for environmental application and water filtration. The presence of transition metals in biochar indicates that they may participate in ageing processes of biochar C in the soil.

Concentrations of Ca, Al, Fe, Ti, and Mn increased, while Si, Mg, Cl, and K decreased or were unchanged after the oxidation treatments. Most alkaline earth and transition metals tend to be very insoluble at high pHs and therefore remained as solid phases adsorbed to or embedded in the biochar surface. Silicon, Cl, and K are soluble in alkaline aqueous
solutions and thus simply solubilized and were washed out of the biochar during the oxidation treatments. Other elements were unchanged or present at very low concentrations.

Table 2.2 Element composition of biochars measured by XRF. Values are reported as mass percent content.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>HT T (°C)</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>500</td>
<td>0.06</td>
<td>4</td>
<td>1.4</td>
<td>0.10</td>
<td>2.1</td>
<td>0.60</td>
<td>1.92</td>
<td>5.9</td>
<td>3.6</td>
<td>0.01</td>
<td>0</td>
<td>0.01</td>
<td>0.06</td>
<td>0</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.06</td>
<td>4</td>
<td>1.6</td>
<td>0.12</td>
<td>2.1</td>
<td>0.64</td>
<td>2.12</td>
<td>6.2</td>
<td>3.8</td>
<td>0.01</td>
<td>0</td>
<td>0.01</td>
<td>0.06</td>
<td>0</td>
<td>0.003</td>
</tr>
<tr>
<td>Aged Alfalfa</td>
<td>500</td>
<td>0.12</td>
<td>7</td>
<td>0.003</td>
<td>0.04</td>
<td>0.0008</td>
<td>0.048</td>
<td>0.34</td>
<td>0.008</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.03</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.13</td>
<td>6</td>
<td>0.003</td>
<td>0.06</td>
<td>0.0007</td>
<td>0.055</td>
<td>0.51</td>
<td>0.038</td>
<td>0.6</td>
<td>0</td>
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<td>0.01</td>
<td>0.05</td>
<td>0</td>
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<tr>
<td>Fresh Maize Stover</td>
<td>500</td>
<td>0.02</td>
<td>1</td>
<td>1.3</td>
<td>0.12</td>
<td>7.5</td>
<td>0.25</td>
<td>0.33</td>
<td>2.9</td>
<td>1.5</td>
<td>0.02</td>
<td>0</td>
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<td>0.011</td>
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<td>0.14</td>
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<td>0.29</td>
<td>0.41</td>
<td>3.0</td>
<td>1.6</td>
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<td>0</td>
<td>0.02</td>
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<td>0.012</td>
<td>0.002</td>
</tr>
<tr>
<td>Aged Alfalfa</td>
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<td>8</td>
<td>1.3</td>
<td>0.14</td>
<td>1.7</td>
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<td>0.01</td>
<td>0.26</td>
<td>7.8</td>
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<td>0.08</td>
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<td>0.12</td>
<td>0.012</td>
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<tr>
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<td>0</td>
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<td>0.04</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<td>0</td>
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<td>0</td>
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<tr>
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<td>0.041</td>
<td>0.011</td>
<td>0.4</td>
<td>0.7</td>
<td>0</td>
<td>0.02</td>
<td>0</td>
<td>0.08</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Aged Maize Stover</td>
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<td>0.04</td>
<td>6</td>
<td>1.1</td>
<td>0.16</td>
<td>5.9</td>
<td>0.19</td>
<td>0</td>
<td>0.19</td>
<td>1.8</td>
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<td>0.30</td>
<td>0.02</td>
<td>0.23</td>
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<td>0</td>
<td>0.03</td>
<td>0</td>
<td>0.13</td>
<td>0.014</td>
</tr>
</tbody>
</table>

2.3.2 FTIR interpretations

Infra-red spectroscopy revealed evidence of surface chemical changes of biochars following the ageing treatments. Spectra of the 500 °C HTT biochars (Fig. 2.1) reveal increased intensity of broad and relatively weak OH stretching bands (3200-3500 cm⁻¹)
following the oxidation treatments indicating the development of alcohol functionality. The carbonyl peak at 1700 cm\(^{-1}\) increased in relative intensity for all 500 °C HTT biochars, suggesting the formation of new carbonyl groups with ageing. The 1590 cm\(^{-1}\) peak associated with oxonium heterocycles increased in prominence after ageing [1]. Aromatic C-C stretching, however, also contributes to this peak and would contribute more with breakdown of large molecular structures due to greater dipole change associated with less restricted systems.

No evidence of hydroxyl character was observed in the FTIR spectra (Fig. 2.2) of the 700 °C HTT biochars either before or after the ageing treatments. Ageing increased absorbance in the functional group region between 1000 – 1800 cm\(^{-1}\) and the fingerprint region between 560 – 960 cm\(^{-1}\). Ageing of the 700 °C HTT alfalfa meal biochar also produced a peak at 1074 cm\(^{-1}\) which is assigned as ether C-O stretching. No evidence of increased intensity for the 1700 cm\(^{-1}\) carbonyl band was observed following ageing. These changes are consistent with a decrease in the degree of aromatic character and development of ether and peroxy-ether moieties manifested as C-O stretching between 1000-1300 cm\(^{-1}\) and out of plane C-O and aromatic C-H deformation bands in the fingerprint region [23]. These data suggest that biochars produced at the different temperatures aged differently.
Fig. 2.1 FTIR spectra of 500 °C HTT biochars. Spectra are labeled as fresh and aged.

Fig. 2.2 FTIR spectra of 700 °C HTT biochars. Spectra are labeled as fresh and aged.
2.3.3 NMR

$^{13}$C NMR spectroscopy of the 500 °C cellulose biochar was performed using a novel multi cross polarization technique (Multi-CP NMR) [17]. Table 2.3 presents the type of C moiety and amounts in the sample for both total and non-protonated C. Spectra are presented in Fig. S2.1. Aromatic C constitutes the largest fraction of C in biochar. Almost half (48%) of total C in the fresh biochar was non-protonated indicating a high degree of condensation of aromatic C in this biochar. There is some evidence of methyl and other sp$^3$ hybridized C as manifested by the 5% alkyl C character in the spectrum of the fresh biochar, which decreased to 4% following the ageing treatment. Carbonyl C and aromatic C bonded to O both increased by 1% with ageing. These changes observed by $^{13}$C-NMR spectroscopy agree with the 2.7% increase in O content determined by elemental analysis (Table 2.1) and are indicative of development of carbonyl, phenol, and pyran-like moieties which is further supported by FTIR evidence (Fig. 2.1). Aromatic C bound to O increased from 8 to 9% on oxidation while non-protonated aromatic C two bond lengths away from O decreased from 4 to 2%. The decrease in aromatic C two bond lengths from O is also consistent with increased ageing of biochar. Aromatic non-protonated C greater than two bond lengths from O remained constant throughout ageing at 32% of total C indicating the recalcitrance of this form of C to ageing. Much of this C may have been deep within biochar and not present at the surface where oxidation and other weathering processes occur.

The Multi-CP technique was not able to yield $^{13}$C NMR spectra of the 700 °C HTT cellulose biochars. The low H content of these biochars make cross polarization inefficient and the conductive nature of the material results in radio frequency induced heating.
Despite dilution in a non-conductive matrix (laponite), these biochars still showed $^1$H (wobble curve) of >2 MHz. The DP NMR spectra of these biochars were acquired using an alternate method and are presented in Fig. S2.2. These spectra exhibit broad peaks centered at 125 ppm, indicating a dominant presence of aromatic C. Additionally, homogeneous peak broadening resulted from rapid (<2 ms) T2 relaxation of $^{13}$C nuclei leading to a broad halo effect making resolution between aromatic and other types of C in these samples impossible. This short T2 is likely a consequence of the electrical conductivity of arene and aromatic C and thus reflect high aromatic C content in biochars produced at 700 °C HTT.

Table 2.3 $^{13}$C Multi-CP NMR results for the 500 °C HTT cellulose biochar. SSB are spinning side bands. bl is bond length.
2.3.4 XPS

X-ray photoelectron spectroscopy previously revealed the presence of oxonium heterocycles in biochar [1]. The C1s spectra of 700 °C HTT biochars derived from maize stover and cellulose, in addition to that of two model compounds, 1,3,5-triphenylbenzene and 2,4,6-triphenylpyrylium bisulphate, are depicted in Fig. 2.3. Carbon bonded to oxonium in the spectrum of 2,4,6-triphenylpyrylium bisulphate manifests as increased intensity ranging from 286.4 to 288.1 eV in binding energy. This phenomenon is absent in the C1s spectrum of 1,3,5-triphenylbenzene which is wholly comprised of aromatic C. Increased intensity in the 286.4 to 288.1 eV region of the C1s spectra of the biochars is consistent with C bonded to oxonium in condensed aromatic structures. Deconvolution of the C1s XPS spectra (Table 2.4) revealed that C represented by the peak maximum at 285 eV decreased following ageing of biochar produced from maize stover which is consistent with a statistically significant decline (p = 0.049) in AEC of this biochar with ageing (Table 2.5). By contrast, 286.4 to 288.1 eV region of the C1s spectra exhibited only subtle change following ageing in biochar produced from cellulose at the HTT of 700 °C, and the AEC of this biochar did not significantly change with ageing (p = 0.50). Precise quantification of the high binding energy component having a maximum at 287.3 eV in the pyrylium standard spectrum and ranging from 287.9 to 288.6 eV in the spectra of the biochars is not possible because the results of the integration are influenced by subtraction of the Shirley background. However, these data show that highly oxidized C, C bonded to oxonium heterocycles, formed in the pyrolysis of cellulose at 700 °C are stable against ageing and that similar structures formed from other components of lignocellulosic biomass; hemicellulose and lignin, are more subject to reduction.
Table 2.4: Deconvolution analysis of C1s spectra for the 700 °C HTT biochars and 2,4,6-triphenylpyrylium bisulphate. FWHM = full width at half maximum. The goodness of fit test statistic is X-square based.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position (eV)</th>
<th>FWHM (eV)</th>
<th>Integrated Area</th>
<th>Composition %</th>
<th>Goodness of Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{23}H_{18}O_{5}S</td>
<td>284.6</td>
<td>1.4</td>
<td>15730.3</td>
<td>67.72</td>
<td>1146.53</td>
</tr>
<tr>
<td></td>
<td>285.0</td>
<td>2.7</td>
<td>6653.79</td>
<td>28.64</td>
<td>1146.53</td>
</tr>
<tr>
<td></td>
<td>287.3</td>
<td>1.1</td>
<td>845.994</td>
<td>3.64</td>
<td>1146.53</td>
</tr>
<tr>
<td>Maize Stover</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>284.5</td>
<td>1.3</td>
<td>13809.1</td>
<td>50.18</td>
<td>1304.3</td>
</tr>
<tr>
<td></td>
<td>285.2</td>
<td>2.7</td>
<td>12342.4</td>
<td>44.85</td>
<td>1304.3</td>
</tr>
<tr>
<td></td>
<td>288.0</td>
<td>3.8</td>
<td>1369.17</td>
<td>4.98</td>
<td>1304.3</td>
</tr>
<tr>
<td>Aged</td>
<td>284.5</td>
<td>1.3</td>
<td>15297</td>
<td>51.98</td>
<td>1384.08</td>
</tr>
<tr>
<td></td>
<td>285.4</td>
<td>2.6</td>
<td>8081.35</td>
<td>27.46</td>
<td>1384.08</td>
</tr>
<tr>
<td></td>
<td>287.9</td>
<td>5.5</td>
<td>6052.09</td>
<td>20.56</td>
<td>1384.08</td>
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<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>284.6</td>
<td>1.2</td>
<td>19509.5</td>
<td>59.77</td>
<td>1432.36</td>
</tr>
<tr>
<td></td>
<td>285.3</td>
<td>2.7</td>
<td>9382.13</td>
<td>28.74</td>
<td>1432.36</td>
</tr>
<tr>
<td></td>
<td>288.4</td>
<td>6.1</td>
<td>3747.53</td>
<td>11.48</td>
<td>1432.36</td>
</tr>
<tr>
<td>Aged</td>
<td>284.5</td>
<td>1.3</td>
<td>15385.7</td>
<td>58.12</td>
<td>1565.34</td>
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<tr>
<td></td>
<td>285.5</td>
<td>2.8</td>
<td>6868.4</td>
<td>25.94</td>
<td>1565.34</td>
</tr>
<tr>
<td></td>
<td>288.6</td>
<td>6.6</td>
<td>4218.86</td>
<td>15.94</td>
<td>1565.34</td>
</tr>
</tbody>
</table>
Fig. 2.3: C1s spectra of select 700 °C HTT biochars and model compounds.

2.3.5 AEC

The AEC of 5 of the 6 studied biochars decreased significantly (p < 0.0001) by an average of 54% following the ageing treatments (Table 2.5). By contrast, the AEC of the 700 °C HTT alfalfa meal biochar was 16.4 % higher following ageing, however based on an unpaired t-test, this difference was not significant (p = 0.20). The decrease in AEC following ageing for the 700 °C HTT cellulose biochar was also not significant, but the
decline in AEC for the maize stover biochar produced at 700 °C was significant. The ageing treatments caused significant decline in AEC in all biochars produced at the HTT of 500 °C.

Table 2.5: AEC (cmol Kg⁻¹ biochar) values for fresh and oxidized biochars measured at pH 6. Data presented as means (standard deviation).

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>HTT (°C)</th>
<th>Fresh AEC</th>
<th>Aged AEC</th>
<th>% Change</th>
<th>2-tailed p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa</td>
<td>500</td>
<td>3.01 (0.279)</td>
<td>1.52 (0.164)</td>
<td>-50.8</td>
<td>0.001</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>700</td>
<td>9.64 (1.08)</td>
<td>11.2 (1.39)</td>
<td>+16.4</td>
<td>0.200</td>
</tr>
<tr>
<td>Cellulose</td>
<td>500</td>
<td>2.63 (0.211)</td>
<td>0.726 (0.359)</td>
<td>-72.4</td>
<td>0.001</td>
</tr>
<tr>
<td>Cellulose</td>
<td>700</td>
<td>18.1 (8.66)</td>
<td>10.5 (1.54)</td>
<td>-42.1</td>
<td>0.209</td>
</tr>
<tr>
<td>Maize Stover</td>
<td>500</td>
<td>3.77 (0.658)</td>
<td>1.72 (0.901)</td>
<td>-54.5</td>
<td>0.033</td>
</tr>
<tr>
<td>Maize Stover</td>
<td>700</td>
<td>13.8 (4.23)</td>
<td>6.88 (0.733)</td>
<td>-50.2</td>
<td>0.049</td>
</tr>
</tbody>
</table>

2.4 Discussion

2.4.1 Generation of \(^1\text{O}_2\)

Conditions during the ageing treatment were alkaline, as the initial aqueous medium was 1 M NaOH; hence added \(\text{H}_2\text{O}_2\) rapidly deprotonated to \(\text{HO}_2^-\). The peroxide anion reacts by one electron transfer with transition metals [24-27], defect sites in aromatic C [9,19], and electron rich basal planes of aromatic C [18,29] to form the peroxide radical.

Equation 1 illustrates this reaction using iron (Fe) as an example of an electron acceptor.

\[
\text{H-O-O}^- + \text{Fe}^{+3} \rightarrow \text{H-O-O}^- + \text{Fe}^{+2} \quad \text{Eqn. 1}
\]

\[
\text{H-O-O}^- + \text{Fe}^{+3} + \text{H}_2\text{O} \rightarrow \text{O-O}^- + \text{H}_3\text{O}^+ + \text{Fe}^{2+} \quad \text{Eqn. 2}
\]

\[
\text{H-O-O-H} + \text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + \text{H-O-O}^- \quad \text{Eqn. 3}
\]

Peroxide radical may further react with transition metals or aromatic C to form \(^1\text{O}_2\) (O-O:) (Equation 2). Upon addition of \(\text{H}_2\text{O}_2\) to biochar slurries, significant effervescence was
observed which indicated formation of O₂ gas. Bottles were left open for 10 minutes to allow most of the gas to escape before the bottles were resealed and returned to the shaker to avoid rupture. The strong alkaline conditions drove formation of \(^1\)O₂ as acid generated (Equation 2) was consumed by \(\cdot\)OH. Generation of H-O• would be favored in neutral or acidic solutions, however the Haber-Weiss reaction (Equation 3) was discouraged by the strong alkaline conditions used in this study. Therefore, we assume that the predominant oxidative specie available in this system was \(^1\)O₂.

![Resonance structures of \(^1\)O₂.](image)

Fig. 2.4: Resonance structures of \(^1\)O₂.

### 2.4.2 Ageing pathways

Three resonance structures exist for \(^1\)O₂ as illustrated in Fig. 2.4. The zwitterion structures of \(^1\)O₂ are highly reactive with olephenic [29] and aromatic C [11,19] as depicted by the scheme of oxidation for naphthalene in Fig. 2.5.
Fig. 2.5: Oxidation of pyrene by $^1$O$_2$.

We use pyrene as an example to demonstrate the reaction of polyaromatic structures with $^1$O$_2$. In structure A, π-electrons in the C-C sp$^2$ bond attract the electropositive oxygen of $^1$O$_2$ resulting in the intermediate (B) in which the α-C attached to the peroxy group becomes sp$^3$ hybridized and the β-C becomes a carbocation. Coulombic forces quickly end this intermediate by formation of the peroxy ether depicted (C). This structure rearranges with ring opening to form a dialdehyde (D). The aldehyde may be further oxidized to various carboxylates or reduced to alcohols, which are present in aged biochar [1,2]. The structure depicted in C, however, can be stable in graphite and graphene.
structures when the β-C is bridging between two aromatic rings; thus it is reasonable to assume that similar peroxy ether structures are also stable in biochars, which are dominated by condensed aromatic C.

Defect sites on graphitic surfaces are known to chemisorb both $^1\text{O}_2$ and triplet O forming stable five and six member ring configurations [30]. Condensed aromatic C also reacts with $^1\text{O}_2$ in a four plus two π electron scheme as depicted in Fig. 2.6. Here we use anthracene as an example of condensed aromatic C. Formation of the six membered ring results in a stable endoperoxide structure [29,31]. This mechanism accounts for the increased O content of the 700 °C cellulose biochar (Table 2.1) and increased C-O stretching character observed in the FTIR spectra for all 700 °C biochars (Fig. 2.2).

The data suggest that more condensed aromatic C changes dominantly through a 4 plus 2 π electron, cycloaddition scheme (Fig. 2.6) [29,31] while less condensed aromatic C oxidizes by a 2 plus 2 π electron scheme (Fig. 2.5). The 2 plus 2 π electron mechanism involves formation of a strained 4 membered intermediate which is inherently more thermodynamically demanding than the concerted reaction. Due to high activation energy requirements, this reaction proceeds with little yield as evidenced by the 2.7% O content increase, yet accounts for the increase in carbonyl character of biochars produced at a HTT of 500 °C. The concerted, 4 plus 2 π electron scheme, which dominated for the more condensed 700 °C biochars, occurred to a greater extent as manifested by the 8.4% increase in O content of the aged 700 °C cellulose biochar and resulted in the formation of stable endoperoxides.
Fig. 2.6: Ageing of aromatic C with endoperoxide formation.

We suggest that the selectivity for ageing pathways is strongly governed by the nucleophilicity of aromatic π electrons and the presentation of bonding orbitals in the reactions between aromatic C and $^1O_2$. More condensed aromatic C may be better able to donate electrons to facilitate 4 plus 2 π cycloadditions. This mechanism implies bonding between the unoccupied molecular orbitals of singlet oxygen and π orbitals of aromatic C, which are perpendicular to the plane of the basal structure, thus steric factors will influence bonding. Greater condensed aromatic C has more planar sheet character and therefore more sites for this reaction pathway. By contrast, the 2 plus 2 π electron scheme is more likely to occur at edge sites and is promoted by the presence of electron donating heteroatoms which are of greater abundance in lower HTT biochars. The decrease in aromatic C two bond lengths away from O presented in the NMR data (Fig. S2.1, Table 2.3) is consistent with the 2 plus 2 π oxidation mechanism.

Superoxide (Fig. 2.7) may also have contributed to the ageing reactions.

Fig. 2.7: Superoxide
Superoxide may form by one electron transfer from radicals found at defect sites in aromatic carbon [9,19] or through the oxidation of transition metals [24-27]. Superoxide reacts rapidly with water to form peroxide anion and hydroxide, however alkalinity in the reaction solution would inhibit this transformation. Itkis and co-workers [32] demonstrated that carbon black is readily oxidized by superoxide resulting in increased carboxylate surface character. Their study was performed in a dry, aprotic, environment. In soils this reaction is anticipated only when biochars are close to the soil surface under low humidity conditions. The strongly alkaline aqueous environment used in our study likely inhibited reaction between biochar and superoxide and the FTIR and $^{13}$C-NMR data do not indicate increased carboxylation of biochar in the ageing treatments.

2.4.3 Impact of oxidation on AEC

Anion exchange capacity in biochar is multicausal but is at least partly attributed to oxonium heterocycles [1]. The decrease in AEC after the ageing treatments (Table 2.5) may be caused by reduction of oxonium to ether. Nucleophilic addition of hydroxide to the $\alpha$-C adjacent to oxonium results in formation of a hydroxyl cyclic ether (Fig. 2.8). Bond hybridization between C-O$^+$ changes from sp$^2$ to sp$^3$ with oxidation of the $\alpha$-C and reduction of the O$^+$ resulting in a hydroxy cyclic ether structure (B) or a pyrone, depending on aromaticity of the ring. The reaction (Fig. 2.8) explains the decrease in AEC (Table 2.5) as a loss of formal charge on the hetero O$^+$ and is consistent with the observed as increased O content (Table 2.1), the decrease in high binding energy C identified by deconvolution of the C1s XPS of the 700 °C HTT maize stover biochar (Table 2.4), and the increase in alcohol character evident in the FTIR spectra of the 500 °C HTT biochars (Fig. 2.1) all of which occurred during the ageing treatments.
Fig. 2.8  Nucleophilic attack resulting in simultaneous reduction of oxonium heterocycle and oxidation of an exposed $\alpha$-C.

The charge on the oxonium heterocycle makes it susceptible to nucleophilic attack when the $\alpha$-C is exposed as described above. When both C atoms directly bonded to $O^+$ are bridging C, however, nucleophilic attack is sterically restricted and reduction of the $O^+$ heterocycle to ether is less likely. Hence presence of $O^+$ surrounded by bridging C in highly condensed aromatic structures may explain the stability of AEC for the 700 °C HTT alfalfa meal biochars (Table 2.4). The high aromaticity of C in the 700 °C alfalfa meal biochar is demonstrated by negligible changes in C, N, and H content after ageing and the lowest H content among the studied biochars (Table 2.1). The study results also suggest that the stability of AEC sites in biochar is related to the biomass feedstock. Cellulose employed in this study was a neat material, consisting of almost pure $\alpha$-cellulose. Maize stover contains more hemicellulose than alfalfa meal and both materials contain cellulose, hemicellulose, and lignin [33,34]. Results indicate that the chemistry and composition of
biomaterials may influence the chemistry of biochar. Further work is needed to explore the transformations of hemicellulose and lignin in pyrolysis to determine if biochar resulting from these materials is different from that derived from cellulose and if such biochar oxidizes by other pathways.

Pyridinium moieties may contribute some pH dependent AEC in biochar [1]. The ageing treatments had negligible effect on N content of biochar derived from alfalfa meal, but substantially reduced N content in biochar derived from maize stover (Table 2.1). This finding suggests that N in biochar derived from the maize stover and alfalfa meal may have been in different functional forms. Unfortunately, the FTIR and NMR spectra provided no clear evidence to either support or reject this hypothesis. From the literature, however, we know that most N in biochars is present as 5 and 6 member heterocycles; specifically pyridine, pyrrole, and pyridone structures [1,35-37]. Of these N heterocycles, only pyridine is a weak base capable of being protonated and contributing to biochar AEC at relevant soil pHs. The pKa of pyridine, however, is 5.2 and we assume that pyridine functional groups in biochar have similar pKa values. If so, then most biochar pyridine groups would have been unprotonated and electrically neutral at the pH (6.0) at which AEC was measured. Furthermore, there is no apparent relationship between N content (Table 2.1) and AEC (Table 2.5) of the studied biochars \((r^2 = 0.01)\) or between the change in N content and the change in AEC due to ageing \((r^2 = 0.24)\). Had all of the N in the alfalfa meal, maize stover and cellulose biochars (average N is 3.40, 0.86, and 0.005\%, respectively; Table 2.1) been present as pyridinium groups; N would have contributed on average of 243, 62, and 0.4 cmol kg\(^{-1}\) to the AEC of the biochars, which averaged 6.3, 6.5, and 8.0 cmol kg\(^{-1}\) (Table 2.5), respectively. The evidence suggests that pyridinium groups
had negligible effect on the AEC of the studied biochars or the change in AEC following ageing. A different result might have been obtained had the study been conducted at a lower pH; as pyridinium groups are anticipated to contribute AEC to biochar under low pH conditions.

Lastly, protonation of the basal planes of aromatic C may also contribute pH dependent AEC to biochar [1,18,38]. Any decrease in aromaticity of biochar during ageing due to endoperoxide formation on polynuclear aromatic surfaces would have reduced the number of sites where protons can be stabilized in the aromatic π ring system. Consistent with this mechanism, we note that there was little change in aromaticity and no loss of AEC for the 700 °C alfalfa meal biochar during the ageing treatments and larger decreases in both aromaticity and AEC among the other biochars during the treatments. Although we were not able to measure the contribution of protonation of aromatic C to biochar AEC in this study; the contribution is believed to be small at pH 6 due to the pH dependence of this mechanism [18,38].

2.5 Conclusions

Biochars produced at a HTT of 700 °C exhibit greater condensed aromatic character than biochars produced at 500 °C HTT; and changed by a concerted 4 plus 2 π electron mechanism yielding endoperoxide surface structures. By contrast, the 500 °C biochars dominantly oxidized by a 2 plus 2 π electron pathway, which led to the formation of more carbonyl and hydroxyl groups on surfaces of these biochars.

Anion exchange capacity of most biochars declined with ageing; exhibiting a mean decrease of 54%. Biochars produced at a HTT of 700 °C had higher AEC values and exhibited greater resistance to loss of AEC during the ageing treatments in contrast to 500
°C HTT biochars. The observed decline in AEC during ageing is partly attributed to the reduction of oxonium heterocycles to pyran structures due to nucleophilic attack on, and oxidation of, non-bridging α-C by OH- groups. Hetero O+ atoms that are adjacent to two bridging aromatic C atoms, which are resistant to nucleophilic attack, are recalcitrant. Thus the 700 °C pyrolysis temperature yielded biochars with more condensed aromatic C that were more likely to have O+ groups with two adjacent bridging aromatic C atoms and hence be recalcitrant to nucleophilic attack and loss of AEC. Other possible mechanisms for the observed loss of biochar AEC during the ageing treatments include the loss of heterocyclic N in pyridinium structures and a decrease in the number of aromatic sites which may abstract protons. Both of these processes, however, are highly pH dependent and believed to contribute little to biochar AEC at pH 6. Further research is needed to accurately quantify the contribution of all three potential sources of AEC in biochars as a function of pH, feedstock biochemistry, and pyrolysis conditions.

2.6 Acknowledgements

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60413992-112883-A, and by the National Science Foundation under Grant Number EPS-1101284.

References


Figure S2.1  Solid state MULTI-CP $^{13}$C NMR spectra of 500 °C HTT biochars derived from cellulose.
Figure S2.2 Solid state $^{13}$C DPNMR spectra 700 °C HTT biochars derived from cellulose.
CHAPTER 3.

ALUMINUM AND IRON BIOMASS PRETREATMENT IMPACTS ON BIOCHAR ANION EXCHANGE CAPACITY

Prepared for *Nature Chemistry*

Michael Lawrinenko\textsuperscript{a1}, Dapeng Jing\textsuperscript{b}, Chumki Banik\textsuperscript{a}, and David A. Laird\textsuperscript{a1}

\textsuperscript{a} Department of Agronomy, Iowa State University

\textsuperscript{b} Materials Analysis and Research Laboratory, Iowa State University

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 improve AEC through the development of metal oxyhydroxide surface coatings.
3.1 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\(^7,\)\(^8\).

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 such as arsenic, chromium, and lead 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\textsuperscript{9}.

We have previously identified three types of functional groups on biochar surfaces that contribute to AEC\textsuperscript{9}: (1) oxonium (O\textsuperscript{+}) 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\textsuperscript{9}. Oxonium heterocycles, by contrast, are a source of pH-independent AEC; however, non-bridging oxonium groups are subject to nucleophilic attack by OH\textsuperscript{-} and rapidly degrade under alkaline conditions\textsuperscript{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, γ-Al\textsubscript{2}O\textsubscript{3} and γ-Fe\textsubscript{2}O\textsubscript{3} (maghemite) have PZNCs at pHs 8.1 and 8.8, respectively\textsuperscript{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 γ-Fe\textsubscript{2}O\textsubscript{3} phases distributed on biochar surfaces\textsuperscript{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 Widélöv (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\textsuperscript{15}. These bonding structures were later demonstrated to be thermally stable up to this temperature\textsuperscript{16}. Studies in organoaluminum chemistry have demonstrated that Al coordinates with alkyl and amine moieties\textsuperscript{17} and that pyrolysis of iminoalane formed stable C-Al-N and C-Al bonding structures with yield promoted by allylation of Al precursors\textsuperscript{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.

3.2 Results

3.2.1 Anion Exchange Capacity and Surface Charge

Table 3.1 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 3.1)\textsuperscript{9}. PZNCs of controls also increased with HTT, consistent with greater oxonium heterocycle content\textsuperscript{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. AEC at pH 8 was observed to increase with PZNC for 700 °C HTT Al, Fe-biochars relative to controls, revealing the influence of metal oxyhydroxide surfaces on these properties.

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 3.1). 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 3.1: Specific surface area, AEC, and PZNC of biochars. AEC reported as mean (standard deviation)

<table>
<thead>
<tr>
<th>HTT (°C)</th>
<th>Treatment</th>
<th>SSA (m²g⁻¹)</th>
<th>AEC (cmol kg⁻¹)</th>
<th>pH</th>
<th>PZNC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>Control</td>
<td>321</td>
<td>7.84(1.74)</td>
<td>6.402(0.344)</td>
<td>8.4</td>
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<tr>
<td></td>
<td>Iron</td>
<td>373</td>
<td>5.23(0.922)</td>
<td>1.18(0.787)</td>
<td>0.360(0.0709)</td>
</tr>
<tr>
<td></td>
<td>Aluminum</td>
<td>247</td>
<td>17.6(2.72)</td>
<td>2.90(1.21)</td>
<td>0.636(0.564)</td>
</tr>
<tr>
<td>700</td>
<td>Control</td>
<td>229</td>
<td>24.2(5.32)</td>
<td>18.7(7.76)</td>
<td>4.11(0.166)</td>
</tr>
<tr>
<td></td>
<td>Iron</td>
<td>331</td>
<td>19.4(1.15)</td>
<td>11.9(0.768)</td>
<td>8.85(2.38)</td>
</tr>
<tr>
<td></td>
<td>Aluminum</td>
<td>305</td>
<td>28.0(2.46)</td>
<td>17.6(3.36)</td>
<td>15.5(5.61)</td>
</tr>
<tr>
<td>500</td>
<td>Control</td>
<td>150</td>
<td>17.5(5.19)</td>
<td>3.77(0.590)</td>
<td>1.05(0.184)</td>
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<tr>
<td></td>
<td>Iron</td>
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<td>13.9(5.58)</td>
<td>4.39(1.28)</td>
<td>1.12(0.778)</td>
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<td>Aluminum</td>
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<td>6.18(1.38)</td>
<td>2.89(0.930)</td>
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<td>Control</td>
<td>259</td>
<td>27.8(8.42)</td>
<td>13.8(3.78)</td>
<td>7.19(1.24)</td>
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<tr>
<td></td>
<td>Iron</td>
<td>263</td>
<td>27.6(5.18)</td>
<td>16.4(2.86)</td>
<td>9.24(2.30)</td>
</tr>
<tr>
<td></td>
<td>Aluminum</td>
<td>309</td>
<td>44.0(2.80)</td>
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<td>0.938(0.302)</td>
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<td></td>
<td>Iron</td>
<td>54</td>
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<tr>
<td></td>
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<td>15.2(4.17)</td>
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<tr>
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<td>Control</td>
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<td>9.64(0.961)</td>
<td>2.15(0.711)</td>
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<tr>
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<td>18.2(0.241)</td>
<td>10.9(2.51)</td>
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<td></td>
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<td>52.9(1.87)</td>
<td>28.9(1.41)</td>
<td>23.5(4.96)</td>
</tr>
</tbody>
</table>

3.2.2 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. 3.1,3.2,S3.1). 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. 3.1. 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. 3.1: SEM micrograph and EDS elemental maps of 700 °C HTT biochar prepared from Al³⁺-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. 3.2). 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. S3.1), suggesting that feedstock properties influence the formation of discrete versus diffuse Fe phases on biochar surfaces during pyrolysis.

Fig. 3.2: SEM-EDS micrograph and elemental maps of 700 °C HTT Fe-cellulose biochar.
3.2.3 XRD Analysis

X-ray diffractometry indicated the presence of sylvite (KCl) and quartz (SiO₂) in samples of 700 °C HTT biochars produced from corn stover and alfalfa meal (Figs. 3.3.3.4). Calcite (CaCO₃) was previously reported in control biochars⁹, 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 S3.1) 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 S3.1). X-ray diffraction patterns of the 700 °C HTT biochar prepared from Al-treated cellulose displayed broad amorphous C reflections⁹ maximized at approximately 23° and 45° 2Θ (Fig. 3.4) but no evidence of inorganic crystalline phases despite containing 2.98% Al (Table S3.1). 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. 3.5).
Fig. 3.3: XRD patterns of 700 °C HTT biochars prepared by slow pyrolysis of Al treated biomass feedstocks. Q = quartz, S = sylvite.
3.3.4 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 S3.2). 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 zerovalent 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. S3.2); 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 $\gamma$-Fe$_2$O$_3$ changes with particle size, evolving from the typical sextet to a doublet of low isomer shift with decreasing particle size (<20 nm)$^{20}$. 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 $\gamma$-Fe$_2$O$_3$.

### 3.3.5 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. S3.3, S3.4). 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. 3.6, 3.7) 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 S3.1), 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. 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. These weak vibrations have been described as characteristic of quinone and semiquinone structures. Change in biochar carbonyl character is observed in association with the metal treatments. Spectra in Figs. 3.6 and 3.7 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. S3.2, S3.3) 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. 3.6); 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\(^{25}\). Thus, the altered alkyl C-O character observed with metal treatments is suggestive that ether structures were involved in the metal bonding.

\(\gamma\)-Al\(_2\)O\(_3\) is the dominant crystalline form of Al\(_2\)O\(_3\) heated above 500 °C\(^{26}\). Evidence of minor hydroxyl stretching in the 3000 to 3700 cm\(^{-1}\) region indicates some hydroxyl character to \(\gamma\)-Al\(_2\)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 \(\gamma\)-Al\(_2\)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. S3.2). Magnetite exhibits some absorbance in the 1000 to 1800 cm\(^{-1}\) functional group region and more in the fingerprint region due to combined Fe\(^{3+}\)-O and Fe\(^{2+}\)-O dipole changes. Though both Al and Fe structures produced in biochar contribute to absorbance in FTIR spectra, lack of IR absorbance by \(\gamma\)-Al\(_2\)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.

Fig. 3.5: FTIR spectra of Al-biochars produced at the HTT of 700 °C.
Fig. 3.6: FTIR spectra of Fe-biochars produced at the HTT of 700 °C.

3.3.6 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. 3.7).27 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. 3.7). 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. 3.8). These results are reported in Table S3.3.

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.\(^{28}\) 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.\(^{28,29}\) Consistent with reported data that demonstrate this phenomenon,\(^{28}\) C content of cellulose control biochars (Table S3.1) clearly show greater C content and FTIR data (Figs. 3.5, 3.6) 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 S3.3), 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.\textsuperscript{30}

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 S3.1) and XRD evidence (Figs. 3.3, 3.4) for quartz in biochars produced from alfalfa and corn stover provide evidence for carbonates and oxides which confound the O\textsubscript{1} component. Biochar produced from cellulose, however, has negligible ash,\textsuperscript{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\textsubscript{1} region, the relatively low amounts of these metals on biochar surfaces (Table S3.4) indicate that observed O is
dominantly organic. The metal treatments effected a transition of $O_1$ surface character to $O_4$; 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, however FTIR data demonstrate a shift in alkyl C-O stretching to higher energy and possible deconjugation of carbonyls. Thus, the oxidation of organic O in biochar by Al and Fe is consistent with oxidation of O associated with alkyl C-O bonds, causing O 1s electrons to have higher binding energy than typically observed in model compounds. This change in the chemical environment of O can only be effected by the abstraction of electron density caused by bonding with a more electronegative atom. Given the lack of F (Table S3.1), this oxidation of O is likely caused by cationic Al and Fe. Deconvolution of the Al 2$p$ and Fe 2$p$ regions yielded single component models with binding energies that ranged from 74.4 to 76.0 eV for Al 2$p$ and 711.3 to 712.2 eV for Fe 2$p_{3/2}$; indicating trivalency of both metals.

Nitrogen on biochar surfaces was incorporated in 5 and 6 member heterocycles (Fig. 3.8), consistent with previous reports. 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 S3.2, S3.3) illustrate that pyridinium moieties do not substantially contribute to biochar AEC.
Figure 3.7: C 1s (left) and O 1s (right) XPS spectra of biochars derived from cellulose.
Figure 3.8: N 1s XPS spectra of biochars derived from alfalfa and corn stover.
3.3 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 Fe$^0$, magnetite, and $\gamma$-Fe$_2$O$_3$ (Table 3.2); 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. 3.1, 3.2). 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,$^{33}$ 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$_2$O groups will carry a formal +1/2 charge. At
pHs below PZNC, Fe and Al oxyhydroxides become increasingly protonated, accruing positive charge,\textsuperscript{34} 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\textsubscript{2}O 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.\textsuperscript{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. 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\textsuperscript{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 mechanism can be beneficial or detrimental to total AEC depending on surface charge density of these phases. 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. 3.2 and S3.1) 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 might 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 3.6, 3.7, S3.3, S3.4). 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 lack for evidence of 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 observed in the SEM-EDS analysis of biochar produced from cellulose. 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 evidence presented for C-O-Al/Fe bonds to biochar surfaces is clear in biochar produced from cellulose due to the lack of inorganic phases. Mineral components in biochar can confound characterization, especially surface studies by XPS. Biochar heterogeneity coupled with myriad surface chemistry add challenge to XPS analysis. Carbon doubly bonded to O such as found in carbonyl functional groups typically exhibits binding energy of 287.8 eV$^{35}$, slightly higher than C singly bonded to oxonium which has
a peak maximum at 287.3 eV. Likewise, calcium carbonate, a mineral found in some biochars, exhibits a C1s peak maximum at 289.4 eV; at binding energies of equivalent strength to chemisorbed water, carboxylates, and esters. Functional groups which share common structures such as esters and ketones which both contain a carbonyl also cannot be differentiated. Similar congruencies are observed with XPS of other elements such as overlap between oxides and alcohols in O 1s spectra. For these reasons, characterization of biochar produced from corn stover and alfalfa was partially confounded and the effects of the metal treatments in these biochars were less obvious.

XPS has been employed in numerous studies to investigate biochar surface chemistry. Lacking, is a representative chemical model which definitively ascertains the types of bonding structures that compose biochar surface chemistry. Biochar heterogeneity coupled with myriad surface chemistry can confound XPS analysis. For example, core C 1s XPS have been inconsistently described by 3 to 5 component chemical models, indicating the number of types of C; C bonded to C, C singly or doubly bonded to O, etc. and their relative amounts. However, chemical models developed on XPS response of model compounds are only valid for simple systems which express sufficient resolution between the spectra of discrete C moieties of known electronic character. The data presented in this study show deviation of biochar XPS from classical chemical models caused by the conjugated π electronic system characteristic of biochar C and differential charging behavior. Additionally, photoemission of other transitions may occur at binding energies of core level emission such as Auger emission of Fe which exhibits similar binding energy to that of core O 1s emission. Such phenomenon may be avoided by using Al \( k\alpha \) radiation instead of Mg \( K\alpha \) radiation. Thus, XPS experimental parameters must be planned with
some knowledge of biochar composition, the impact of surface heterogeneity on sample response, and knowledge of other surface properties to properly elucidate biochar surface chemistry. Characterization by FTIR spectroscopy accompanies similar complications; with broad distributions of Fermi levels which contribute to peak broadening, vibrations of different bonds at similar energy levels, and combination overtone overlapping; all confounding spectral interpretations. Lacking complementary data such as XPS, FTIR, and surface charge characteristics would have yielded interpretations different from what we report. Hence, we suggest biochar characterization to be performed on simple systems with known compositions, using a holistic analytical approach that provides complementary evidence while indisputably differentiating bonding structures.

There exists concern for environmental hazards resulting from application of biochars having C-Cl moieties to soil\textsuperscript{43}. Cellulose-derived biochar was dominantly composed of C, H, and O and additionally Al or Fe and Cl with metal pre-treatment (Table S3.1). The C-Cl bond exhibits a strong stretch at 830 cm\textsuperscript{-1} in FTIR spectra of model compounds\textsuperscript{23} and can shift to lower frequency with electron donating neighbors such as O as in the case of \textit{p}-chloranil\textsuperscript{44}. However, IR characterization of C-Cl moieties in these biochars is confounded by aromatic C-H bending and the broad Al-O vibrations, which also occur in the fingerprint region. No evidence of C-Cl bonds was present in the spectra of the metal treated biochars and XPS did not detect Cl on biochar surfaces. Despite Cl levels as high as 10.4\% (Table S3.1), we assume that most if not all of the Cl was present as chloride. Further work is necessary to assess environmental toxicity of biochars produced by metal chloride treatments.
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 hinder 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.

3.4 Methods

3.4.1 Biochar Preparation

Biochars were prepared from alfalfa meal, corn stover, and cellulose; which were wetted with FeCl$_3$ or AlCl$_3$ 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 N$_2$ 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.

3.4.2 Biochar Characterization

Specific surface area was measured by N$_2$ 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).⁴⁵ 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° 20 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 ⁵⁷Co(Rh) source at ambient temperature. The driver velocity was calibrated using α-Fe foil and all isomer shifts
(IS) are quoted relative to the α-Fe foil at RT. MossA software was used to analyze the spectra\textsuperscript{46}. 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. Complete description of these techniques are fully provided in the Supplemental Information.

References


### 3.5 Acknowledgements

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APPENDIX B. SUPPLEMENTAL INFORMATION TO CHAPTER 3

Materials and Methods

Biomass preparation

Biomass materials (alfalfa meal, corn stover, and cellulose) 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 pyrolyzed 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.

Pyrolysis

Biochars were produced by slow pyrolysis using a programmable muffle furnace that heated to highest treatment temperatures (HTTs) of 500 °C and 700 °C under N₂ purge using the method described in Lawrinenko and Laird (2015).

Elemental analysis

Biochar samples were analyzed in duplicate to determine C, N, H, and S contents using an Elementar Vario Micro Cube thermal combustion analyzer. A Philips PW 2404 X-ray fluorescence (XRF) spectrometer was used for bulk chemical analysis.
The spectrometer was equipped with a rhodium X-ray tube and was operated at 3600 Watts. The spectrometer was flushed with helium (He) gas during all measurements. All measurements were corrected for tube drift by monitoring a reference sample (AUSMON-silicate minerals reference monitor). Prior to analysis, biochar samples were ground in a SPEX shatterbox puck mill for two minutes. Two grams of ground sample were placed into a disposable sample cup and sealed with polypropylene film (6-μm thick). Calibration standards were prepared by mixing the 700 °C cellulose control biochar (0.92% ash) and the 700 °C alfalfa meal biochar (30.89% ash) (Lawrinenko and Laird, 2015) with known quantities of reference standards, specifically NIST 1633a, NIST 2691, ACS Grade potassium chloride, USGS Nod-A-1, NIST 2910 and AWP Std I.

**AEC and Specific Surface Area analysis**

Anion exchange capacity was measured in triplicate using chloride for bromide exchange. Biochar samples (1g, accurately weighed) were equilibrated at pH 6, saturated with 1 M KBr, rinsed to remove excess KBr, then washed with 2.5 M CaCl₂ to displace the retained Br⁻. The extract was diluted to a known volume and a subsample of the solution was analyzed for Br 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. A complete description of the AEC method was given by Lawrinenko and Laird (2015).¹
Specific surface area was measured using the Brunauer–Emmett–Teller (BET) method using a NOVA 4200e gas adsorption analyzer (Quantachrome Instruments). High purity nitrogen (>99.999%) gas was used as the adsorbent. The BET regression analysis was performed over five relative pressure points ranging 0.05 to 0.30.

**Point of Zero Net Charge**

Point of zero net charge (PZNC), was determined as the pH of zero salt effect using a batch method adapted from Zelazny et al. (1996). In this method, the pH at which exchangeable proton or hydroxide is independent of ionic strength reflects the isoelectric point of the surface. Biochars were first sieved to isolate the < 0.5mm fraction and then pretreated to remove carbonates and to Na⁺ saturate all sites capable of cation exchange. 20 g biochar samples were combined with 100mL 0.1 M HCl and 0.1 M NaCl in plastic bottles, capped, and shaken on an oscillating shaker for 24 hours, then filtered through 0.45 μm nylon filters, and washed with DI water until filtrate produced no visible evidence of a AgCl precipitate when AgNO₃ test solution was added to the filtrate, then dried at 65 °C for 5 days in a convection oven. In PZNC determination, 0.36 g subsamples of biochar were accurately weighed into 20 mL plastic vials and combined with 18 mL of NaCl solutions for each of 3 ionic strengths (0.05, 0.01, 0.002 M) adjusted to specific pHs ranging pH 2 to 10 for 13 total pH points, shaken for 4 hours, after which pH was adjusted to pH of the fresh NaCl solution prior to exposure to biochar using standardized HCl or NaOH solutions. PZNC was estimated from the point of zero salt effect; the pH at which the plots of moles of protons or hydroxide added versus pH converge.

**Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDS) Analysis**
Biochar samples were washed with CaCl₂ (Al biochars) or KBr (Fe biochars) solutions, filtered on 0.45 μm Teflon filter paper, and washed with DI water until the rinsate conductivity was that of Milli-Q water, 18 μSdm⁻¹. SEM mounts were prepared by attaching a 5 mm silicon wafer to the top of a 0.5 inch carbon stub using double sided graphite tape. A drop of biochar suspension was then placed on the wafer and samples were dried in a desiccator. Microscopy was performed with a 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.

X-ray Diffraction Analysis

Diffraction patterns of biochar samples were collected from 10 to 90° 2θ with a Siemen D5000 x-ray diffractometer using Cu Kα 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. A scintillation counter detector with fixed 0.15° divergence and 1.0° anti-scattering slits was used. Random powder mounts of biochars were analyzed at ambient temperature and humidity. Patterns were analyzed using JADE v9.0.

Mössbauer Spectroscopic Analysis

Spectral measurements were performed using a SEE Co. conventional, constant acceleration type spectrometer in transmission geometry with an $^{57}$Co(Rh) source at ambient temperature. Biochar samples were prepared as described for XRF analysis. The sample holder comprised two nested white Delrin cups. Sample was placed uniformly on the bottom of the larger cup and was held in place by a smaller cup. The driver velocity was calibrated using α-Fe foil and all isomer shifts (IS) are
quoted relative to the α-Fe foil at RT. MossA software (Prescher et al., 2012) was used to analyze the spectra.

**FTIR Analysis**

Spectra of biochar samples were obtained with a Nicolet 560 Magna - IR spectrophotometer using the diffuse reflectance accessory. Spectra recorded in absorbance mode from 4000 to 400 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) and a total of 200 scans were averaged to produce the final spectrum. Biochars (1% wt/wt) were co-ground with spectroscopy grade KBr for 2 minutes in a SPEX 5100 mixer mill prior to analysis.

**XPS analysis**

Spectral measurements were performed using a Physical Electronics 5500 Multitechnique spectrometer with a standard aluminum source operated at 250 W. Analysis spot size was 2mm x 2mm. Samples were mounted on double sided tape. Spectra were shifted relative to the carbon maximum at 284.7 eV. Deconvolution of spectra was performed with Gaussian fit and Shirley background using Casa XPS.
Table S3.1: Elemental analysis of biochars. Values reported as mass percent and HTT (°C).

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Table S3.2: Iron assay by Mössbauer spectroscopic analysis. Magnetite A – Fe(III), Magnetite B – Fe(II), γ-Fe$_2$O$_3$ is paramagnetic, α-Fe$_2$O$_3$ is diamagnetic, amorphous.

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<th>INT (%)</th>
<th>QS</th>
<th>BHF (T)</th>
<th>Iron Specie</th>
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<td>-0.03(2)</td>
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<td>0.68(3)</td>
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<tr>
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<td>1.2(3)</td>
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<td>48.6(6)</td>
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<td>0.320(7)</td>
<td>0.73(2)</td>
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<tr>
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<tr>
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<td>0.33(4)</td>
<td>0.6(2)</td>
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<td>0.37(1)</td>
<td>0.77(4)</td>
<td>52(3)</td>
<td>0.87(2)</td>
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</tr>
<tr>
<td></td>
<td>-0.05(8)</td>
<td>1.2(2)</td>
<td>28(3)</td>
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<td>zero valent iron</td>
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<tr>
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<td>0.28(2)</td>
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<td>49.11(4)</td>
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Table S3.3: XPS analysis of biochars. Deconvolution based on chemical models indicated in top row with atom in bold representing chemical environment of the specified element. Values presented represent atomic percent detected on biochar surfaces. Al = aluminum biochars, Fe = iron biochars, C = control biochars, Ar N₆ = pyridinium, Ar N₅ = pyrrole, C=ON₆ = pyridone. O_I = inorganic O + alcohol O, O_II = carbonyl O. H₂O = O associated with water.

<table>
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<tr>
<th>Chemical Model</th>
<th>C-C</th>
<th>C-O</th>
<th>C=O</th>
<th>C:H₂O</th>
<th>O_I</th>
<th>O_II</th>
<th>H₂O</th>
<th>ArN₆</th>
<th>Ar N₅ / C=ON₆</th>
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<td>289.8</td>
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<td></td>
<td></td>
<td></td>
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<td>4.6</td>
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Table S3.4: Elemental composition of biochar surfaces measured by XPS.

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Figure S3.1: SEM-EDS micrograph and elemental maps of 700 °C HTT Fe-alfalfa biochar.
Figure S3.2: Mössbauer spectra of 700 °C HTT Fe biochars and magnetite reference standard.
Figure S3.3: FTIR spectra of Fe biochars produced at the HTT of 500 °C.
Figure S3.4: FTIR spectra of Al biochars produced at the HTT of 500 °C.
CHAPTER 4.

SUSTAINABLE PYROLYTIC PRODUCTION OF ZEROVALENT IRON

Accepted: ACS Sustainable Chemistry and Engineering,
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Michael Lawrinenko, David A. Laird and (Hans) van Leeuwen

Abstract

Pyrolysis of biorenewable feedstocks and iron oxides is potentially a greener and more sustainable pathway to producing zerovalent iron (ZVI) for environmental rehabilitation. The resulting biochar-zerovalent iron (BC-ZVI) also shows improved remediation kinetics of trichloroethylene over conventional ZVI. Understanding the transformations of iron to ZVI and the influence of feedstock chemistry on ZVI is critical to the production of BC-ZVI and has not been reported previously. BC-ZVI production was studied by one-step pyrolysis of cellulose, corn stover, dried distillers’ grain, red oak, and switchgrass pretreated with FeCl₃. Pyrolysis at 900 °C effectively reduced Fe to ZVI with most feedstocks, however, the association of silicon (Si) and phosphorus (P) with Fe resulted in formation of fayalite and Fe phosphates and phosphides, which limited ZVI production efficiency and/or facilitated corrosion of ZVI. Dispersion of ZVI phases on biochar surfaces and association with Si facilitated oxidation of ZVI due to greater accessibility to
oxygen and enhanced corrodibility of ZVI in association with fayalite. Feedstocks low in Si and P such as cellulose and red oak yield BC-ZVI suitable for environmental applications.

Keywords

Biochar zerovalent iron, pyrolysis, cellulose, corn stover, dried distillers’ grain, red oak, switchgrass, trichloroethylene remediation

4.1 Introduction

Trichloroethylene (TCE) is a toxic, anthropogenic contaminant known for its adverse human health effects, environmental persistence, and the fact that some of its degradation byproducts are equally or more toxic than the parent compound; markedly challenging remediation.1 With 427 superfund sites in the United States having groundwater contaminated by TCE,2 contamination has become a national concern as these sites are mostly near urban populations, which require safe drinking water. In-situ aquifer and soil remediation by zerovalent iron (ZVI) nanoparticles3-6 and larger iron (Fe) filings installed as permeable reactive barriers (PRBs)7,8 have been demonstrated to effectively decontaminate TCE from soil and groundwater. This remediation technique employs a redox mechanism by which TCE is reductively dechlorinated to hydrocarbon and chloride with the concomitant formation of Fe oxides. While ZVI soil application is an effective remediation practice, implementation is limited due to high material cost. Further, current ZVI production methods carry a significant climate impact with almost 97% of greenhouse gas emission and environmental impacts associated with remediation attributed to ZVI production.9 The need for environmental protection while cleaning
up contaminated soil and water call for more sustainable and environmentally responsible ways to produce ZVI for remediation.

Recent research has demonstrated that ZVI composited with pyrogenic carbon (C) as found in biochar and activated C exhibits better decontamination kinetics than ZVI alone.\textsuperscript{10,11} The researchers used borohydride to reduce dissolved Fe onto biochar and activated carbon surfaces using borohydride.\textsuperscript{12-14} ZVI nanoparticles are also produced by borohydride reduction of Fe, and while nanoparticles also demonstrate rapid decontamination kinetics, their effects are short-lived.\textsuperscript{15,16} Use of borohydride to produce ZVI for environmental use is expensive\textsuperscript{17} and impractical, because of the large chemical demand and generation of borate waste streams. Borohydride production is inherently energy intensive and most processes employ petrochemicals.\textsuperscript{18} Thus, borohydride based ZVI production bears a significant climate impact. Milling of steel into filings also requires complex manufacturing processes and steel produced by conventional methods requires substantial energy and coal. An alternative approach to produce ZVI for environmental remediation is one-step pyrolysis,\textsuperscript{10} in which an Fe-rich source is mixed with biomass and then cofired under low-oxygen conditions. The resulting product material generally contains nanometer- to micrometer-sized ZVI phases composited with biochar: the solid residue of pyrolyzed biomass. This material has been described as BC-ZVI.\textsuperscript{10}

One-step pyrolysis\textsuperscript{10} is potentially a practical and economic pathway to produce affordable ZVI for remediation purposes, as biorenewable, agricultural residues and iron oxides such as dirty or otherwise non-recyclable steel scrap and low-grade Fe ores could be used as feedstock materials. Lifecycle analyses of biochar production
show that manufacture can be carbon neutral\textsuperscript{19,20} and that carbon sequestered in soil with biochar application reduces the climate impact associated with steel production.\textsuperscript{21} Thus, pyrolysis-based production of ZVI is also potentially a greener and more sustainable approach for an environmental remediation product compared to conventional methods.

Only one prior study\textsuperscript{10} has shown that ZVI can be produced in the pyrolysis of biomass, however, reduction of Fe was performed from the ferrous state in combination with coir pith, a relatively clean biomass used for activated carbon precursor due to its low mineral content. While some wood species also exhibit low mineral content, most biomass such as agricultural residues from grain production or dedicated bioenergy crops contain significant mineral fractions and are far more abundant than limited wood species. Production of ZVI from a variety of feedstocks would ensure adequate supplies of ZVI if produced from locally sourced biomaterials and Fe oxide sources, thus extending access to remediation. Lacking still is an understanding of the transformations of Fe to ZVI in biomass pyrolysis and how the composition of different biomass feedstocks affects the reduction of Fe and the quality of ZVI in biochar.

We hypothesized that ZVI can be produced from various biomass feedstocks during pyrolysis and that Fe may associate with certain elements inherent to biomass. Additionally, some Fe minerals that form in pyrolysis may alter the quality of ZVI, thus certain biomass feedstocks may not be suitable for the pyrolytic production of ZVI. The influence of temperature and feedstock composition in producing ZVI by pyrolysis of biomass mixed with ferric oxides or halides have also
not been reported. This study examines the production of BC-ZVI composites from a variety of biomass feedstocks pretreated with ferric chloride (FeCl₃) and reports the influence of pyrolysis temperature and feedstock chemistry on the resulting pyrolytic mineralogies.

4.2 Experimental

4.2.1 Biochar Preparation

Biomass materials (pyrolysis feedstock) used in this study included cellulose, corn stover, dried distillers’ grain (DDG), red oak, and switchgrass. The cellulose was purchased (α-cellulose, Sigma-Aldrich) and used as received. Corn stover was obtained locally and ground in a Wiley Mill. DDG was a course dry granular material obtained from Lincolnway Energy, LLC (Nevada, IA) and used as received. Switchgrass was obtained in bale form from a local source in Story County, IA. Bales were shredded using a Vermeer BP8000 bale shredder to reduce grass to 6-12" strands and subsequently milled using an Artsway, 60hp 26" hammer mill equipped with a 1/4" screen. Red oak was obtained locally in 3/4" chips and milled with the same hammer mill equipped with a 1/8" screen.

To produce biochars, the ground feedstock materials were wetted with 1 M FeCl₃ at 10% weight of metal to weight of air-dry biomass (200 g). FeCl₃ was selected as a model Fe³⁺ source to study the reduction of Fe to ZVI and is fully soluble in water, to effectively distribute Fe in biomass. Additional water 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 one day, transferred to a stainless steel box, and subsequently slow-pyrolyzed using a muffle furnace that
heated to highest treatment temperatures (HTTs) of 700 °C and 900 °C under a 40 ml·min\(^{-1}\) N\(_2\) purge. Control biochars were produced from the same raw biomass sources. Pyrolysis generates myriad noxious gases which can be harmful to health, thus it is imperative that pyrolysis be performed in a hood or otherwise well-ventilated work area.

### 4.2.2 Elemental Analysis

Elemental analysis was performed as described by Lawrinenko et al. (2016).\(^{22}\) Assay of C, N, H, and S contents was performed in duplicate using an Elementar Vario Micro Cube combustion analyzer. A Philips PW 2404 X-ray fluorescence (XRF) spectrometer was used for the bulk chemical analysis. The spectrometer was equipped with a rhodium X-ray tube operated at 3600 W and was flushed with helium gas during all measurements. The XRF measurements were corrected for tube drift by monitoring a reference sample (AUSMON-silicate minerals reference monitor). To prepare samples for the XRF analysis, biochar samples (5-10 g) were ground in a SPEX shatterbox puck mill for two minutes and 2 g of ground sample were placed into a disposable sample cup and sealed with polypropylene film (6-μm thick). Calibration standards were prepared by mixing biochar produced from cellulose at 700 °C (0.92% ash) with known quantities of reference standards, specifically NIST 1633a, NIST 2691, USGS Nod-A-1, NIST 2910, AWP Std I, and ACS reagent grade chemicals.

### 4.2.3 X-ray Photoelectron Spectroscopic (XPS) Analysis

Spectral measurements were performed using a Kratos Amicus/ESCA 3400 instrument using the air-sensitive accessory. Samples of fresh biochars were ground
in a ball mill and transferred to the air-sensitive sample holder while under a nitrogen atmosphere. Analysis was performed with 240 W of unmonochromated Mg Kα x-rays, and photoelectrons emitted at 0° from the surface normal were energy analyzed using a DuPont type detector. The pass energy was set at 75 eV. Data analysis was performed using CasaXPS v 2.3.16 pr1.6 and a Shirley baseline was removed from all reported spectra.

4.2.4 X-ray Diffraction (XRD) Analysis

Diffraction patterns of biochar samples were collected from 10 to 90° 2θ with a Siemens D5000 x-ray diffractometer using Cu Kα 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 s per step. Fixed 1.0° divergence and 3.0° anti-scattering slits were used with a scintillation counter. Random powder mounts of biochars ground in an agate mortar were analyzed at ambient temperature and humidity. The XRD patterns were analyzed using JADE v9.0. Stability of ZVI in biochars was studied by XRD analysis of freshly prepared biochars and subsamples of biochars exposed to ambient air and humidity in a laboratory environment after one week and one month.

4.2.5 Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDS) Analysis

Samples were mounted to the top of a 12.5 mm carbon stub using double-sided graphite tape by compressing the taped stub against a subsample of biochar. Microscopy 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. Elemental maps were obtained by energy dispersive x-ray analysis using an Oxford Aztec EDS.

4.3 Results and Discussion

4.3.1 Feedstock chemistry and pyrolysis temperature impacts on iron reduction

Pyrolysis temperature and feedstock composition influenced the Fe mineralogies that formed in biochar. Reduction of Fe was achieved to different degrees depending on associated anions, the thermal stability of lattice structures, and overall reducing conditions that were present during pyrolysis. Successful formation of ZVI was achieved for biochars produced from cellulose, corn stover, red oak, and switchgrass pyrolyzed at 900 °C HTT as indicated by the 110, 200, and 211 XRD reflections of ZVI depicted in Figure 4.1. Magnetite was the dominant form of Fe in biochars produced at 700 °C HTT. However, some evidence of ZVI formation was also observed for biochars produced from cellulose, corn stover, and red oak pyrolyzed at 700 °C HTT. No evidence for ZVI was observed for biochar produced from switchgrass at 700 °C HTT. The XRD results show no evidence of ZVI formation during pyrolysis of FeCl$_3$ treated DDG at either 700 °C or 900 °C HTT (Figs. 4.1 and S4.6). In general, the XRD results indicate more Fe reduction with greater transformation to ZVI at 900 °C than 700 °C HTT, however the results also show that feedstock properties influence the formation of ZVI during pyrolysis.

Transformation of Fe$^{3+}$ to ZVI is a reductive process that requires oxidation of an associated anion or exchange of the anion with, and oxidation of, another element such as C. This reduction reaction occurs during pyrolysis of Fe$^{3+}$ treated biomass (Figure 4.1) and could be driven by the concomitant oxidation of biomass C to CO$_2$ or CO. Additionally, during biomass pyrolysis reducing gases such as H$_2$, CH$_4$, and CO are evolved, which may
also facilitate Fe reduction. Hence, variability in the production of reducing gases and/or the rate of electron transfer from reducing gases or solid C phases to Fe$^{3+}$ during pyrolysis are likely responsible for the observed differences of ZVI formation for different feedstocks and HTTs.

XRD peaks for fayalite (Fe$_2$(SiO$_4$)), quartz (SiO$_2$), hematite (Fe$_2$O$_3$), and sylvite (KCl) were identified in the diffraction patterns for biochars produced from corn stover, red oak, and switchgrass along with small peaks for calcite, forsterite (Mg$_2$(SiO$_4$)), and potassium carbonate. Interpretations of the diffraction patterns are supported by bulk chemical analysis (Table S4.1). In general, greater diversity in mineralogy corresponded with diverse elemental composition. The presence of fayalite in biochars produced from corn stover, red oak, and switchgrass demonstrates a tendency for Fe to associate with silicon (Si) during pyrolysis.

**4.3.2 Iron reduction in pyrolysis**

Fayalite is known to be a byproduct of iron smelting as quartz sands were historically used as a fluxing agent in early iron production. Its formation and thermodynamic equilibria in association with iron phases has been studied extensively. Fayalite forms due to coordination of ferrous iron with silicate and forms a solid solution with ZVI. Phase diagrams of iron illustrate the relationships between ZVI and oxides of Fe as a function of temperature, pressure, and O$_2$ fugacity. Wüstite (FeO) is a metastable transition phase of Fe that dominates high temperatures over a range of O$_2$ fugacity at low pressure. Fayalite and magnetite form in conjunction with ZVI due to the solubility of these mineralogies with the wüstite phase, which forms at high temperatures. Instability of wüstite at low temperature, pressure, and oxygen fugacity drives phase transformation to ZVI and
magnetite. Exsolution of fayalite and magnetite phases from solid solution with wüstite occurs during cooling and depends on the stoichiometry and long range crystalline order of wüstite. The relative amounts of fayalite, magnetite, and ZVI that formed in the production of BC-ZVI are thus controlled by Si-content and the abundance of oxidizing gases such as O₂ in association with wüstite at high temperatures. The absence of oxidants regulates the stoichiometry of wüstite, which transforms to ZVI and magnetite upon cooling. Thus low O₂ and low Si-content of the feedstock favor a higher yield of ZVI.

4.3.3 Influence of phosphorus

Biochar derived from DDG was rich in P and K, with control 700 °C HTT biochar containing almost 22.5% P and 55% K by mass. As a result, most of the Fe in the FeCl₃ treated DDG biochar was associated with these elements, and there was no evidence of ZVI in either the 700 °C or 900 °C HTT DDG biochars. Rather the XRD patterns for the of 700 °C HTT DDG biochar exhibited evidence for iron carbide (Fe₃C), goethite (é-FeO(OH)), potassium iron phosphate (K₂Fe₂P₈O₂₄), and barringerite (Fe₂P). Similarly, 900 °C HTT DDG biochar exhibited diffraction evidence for Fe₃C, é-FeO(OH), Fe₂P, and schreibersite (Fe₃P).
Fig. 4.1: XRD patterns of fresh BC-ZVI composites. C = Calcium Oxide, Z = ZVI, Q = Quartz, M = Magnetite, S = Sylvite, B = Barringerite, Sc = Schrebersite, F = Fayalite, K = K$_2$Fe$_2$P$_8$O$_{24}$.

A transition occurred in heating from 700 °C to 900 °C. K$_2$Fe$_2$P$_8$O$_{24}$ which formed in biochar at 700 °C HTT thermally decomposed at higher temperatures yielding Fe$_3$P, potassium oxide (K$_2$O), and sylvite (KCl) in 900 °C HTT DDG biochar.

Additional evidence of this phosphate to phosphide transformation is observed in the Fe 2$p$ XPS of these biochars (Fig. 4.2). The high-spin (HS) character of Fe observed in Fe 2$p$ spectra of 700 °C HTT DDG biochar is consistent with high-field ligands, which contribute paramagnetic character to Fe minerals. The Fe 2$p$ spectrum of 900 °C HTT DDG biochar does not exhibit evidence of HS iron. Iron observed in both spectra is trivalent, ferric iron; however, the lower signal intensity of the higher binding-energy shoulder observed in the 2 $p_{3/2}$ spectrum of the 900 °C HTT DDG biochar is due to
increased crystal field splitting when Fe is associated with phosphide as opposed to phosphate.

**Fig. 4.2:** Fe $2p$ XPS of biochars derived from cellulose and DDG.
This difference in 2p_{3/2} spectra is likely due to thermal decomposition of phosphate, resulting in Fe coordinated with phosphide versus an oxygen atom in phosphate. Iron observed in the Fe 2p spectra of biochar produced from cellulose is likewise ferric iron, illustrating oxidation of the exterior surfaces of Fe phases. No differences are observed in the Fe 2p spectra of biochar produced from cellulose due to the stability of oxides that formed on ZVI phases in this biochar.

### 4.3.4 Influence of silicon on iron corrodibility

We have shown that BC-ZVI composites can be produced from a variety of feedstocks, however, not all feedstocks yield stable ZVI appropriate for direct soil application due to rapid corrosion of ZVI in some biochars (Figs. S4.1-S4.5). Corrosion of Fe is described as a shell-core process by which oxidation occurs from the outside of a particle and proceeds toward its center; requiring transport of electrons to an acceptor, typically O_2, with diffusion of the latter into the structure of ZVI.\(^{31,32}\) The electrical conductivity of Fe oxides that form with oxidation and the diffusivity of O_2 both influence the rate at which Fe corrodes. Examination of the full width at half maxima of 001 XRD reflections of ZVI among BC-ZVI produced from cellulose, corn stover, red oak, and switchgrass reveals consistent size of coherent diffracting domains among all biochars (Fig. S4.6), which merely reflects statistically similar long range order of ZVI and does not reveal information about the size of discrete phases or aggregates. However, Fe in biochar produced from corn stover and switchgrass oxidized in a laboratory environment within one week as evidenced by loss of fayalite and ZVI reflections. Intensities of reflections characteristic of quartz and sylvite concomitantly increased, indicating that mineral structures that had formed during pyrolysis containing Si and Cl decomposed to these minerals accompanied
by the oxidation of Fe (Figs. S4.2, S4.5). By contrast, ZVI in biochar produced from cellulose and red oak were stable against oxidation in the same laboratory environment for one month (Figs. S4.1, S4.4). BC-ZVI is intended to provide a source of corrodbile Fe for environmental applications, however, corrosion that occurs too quickly would not be a practical electron source for remediation of TCE in soils.

The contrasting corrosion rates of ZVI in biochar produced from corn stover and switchgrass versus that of cellulose and red oak is related to the structure and distribution of ZVI phases. SEM micrographs and corresponding elemental maps of Fe, Si, and chlorine (Cl) in fresh 900 °C HTT BC-ZVI are presented in Fig. 4.3. Fe L series maps of biochar produced from corn stover and switchgrass reveal dispersion of Fe in these biochars. By contrast, Fe in biochars produced from cellulose and red oak was aggregated in particles (~1 to 10 µm diameter). Assuming that the diffusion of O₂ and electron transfer are the rate limiting steps for the corrosion of ZVI, then the aggregation of ZVI crystallites in the red oak and cellulose biochars and the dispersion of ZVI in the corn stover and switchgrass biochars explains the different observed rates of corrosion.

Distributions of Fe and Si observed in the elemental maps of biochars (Fig. 4.3) produced from corn stover and switchgrass support the identification of fayalite and quartz in the XRD patterns of these biochars, with partial correlation indicating partial association between these elements (Fig. 4.1). Fayalite is electrically conductive and increasing fayalite concentrations exsolved from ZVI phases has been shown to increase electrical conductivity of the composite. Thus, fayalite may have facilitated corrosion of ZVI in the corn stover and switchgrass biochars by enhancing electron transport during oxidation and also increasing defect site population in the ZVI continuum. Oxidation of both fayalite
and ZVI is observed as transformation to quartz and hematite as revealed by XRD patterns of 900 °C HTT BC-ZVI produced from corn stover and switchgrass (Figs. S4.2, S4.4). Thus, oxidation of fayalite and its association with ZVI, coupled with dispersion of ZVI phases likely caused the rapid corrosion of ZVI in BC-ZVI, indicating the need to select feedstocks low in Si for producing BC-ZVI with practical corrosion characteristics suitable for environmental use.

4.3.5 Fate of chlorine in pyrolysis

Chlorine was present in all biochars, with increased content in biochars produced from FeCl$_3$ treated biomass. Some Cl was associated as KCl, sylvite (Fig. 4.1), however much of it developed as FeCl$_2$ in 700 °C HTT biochars from the decomposition of FeCl$_3$. As the temperature exceeded the melting point of FeCl$_2$ (677 °C), it is likely that the liquid coated rigid surfaces with thin films that recrystallized upon cooling. Biochars produced at 900 °C from red oak and cellulose exhibited much lower Cl content compared to biochars produced from the other feedstocks (Table S4.1). The data suggest that FeCl$_2$ further decomposed at temperatures above 700 °C, with Cl volatilizing from the solid phase in the absence of suitable cations with which to coordinate, and that residual Cl remaining in biochar became associated with other elements as chloride salts. Here, we observe that Cl predominantly associated with K to form sylvite.

Further evidence for the decomposition of FeCl$_2$ at temperatures approaching 900 °C is observed in the Cl K series elemental maps. Chlorine is well dispersed across biochar surfaces as seen in these maps (Fig. 4.3). Association of Cl with Si observed in elemental maps of switchgrass BC-ZVI is inconsistent with patterns observed in corresponding maps of corn stover BC-ZVI: maps of Cl and Si in corn stover BC-ZVI show lack of one element
when the other is present and maps of the switchgrass BC-ZVI show a Si-rich region in the left side of the image and uniform distribution of Cl over the entire map. The stoichiometry of Fe and Cl in BC-ZVI produced from cellulose and red oak indicates insufficient Cl for significant presence of FeCl$_2$. The distribution of Cl in these BC-ZVI also do not evince association of Cl to Fe in the elemental maps. The elemental content of alkali, alkaline earth, and transition metals in these biochars can easily account for Cl as chlorides. Lastly, Cl 2 $p_{3/2}$ XPS of biochar produced from cellulose and DDG reflect two-component distributions with peak maxima ranging 198.5 to 199.9 eV, consistent with chlorides. These spectra are not reported here due to low signal to noise ratio and, hence poor quality of Cl 2 $p_{3/2}$ spectra of the BC-ZVI derived from cellulose. The chloride character of Cl in biochar produced from DDG, elemental analysis (Table S4.1) which shows stability of chloride compounds manifested as a minor change in Cl content (35.6 % to 30.2%) between the two pyrolysis temperatures, trivalent Fe observed in the Fe 2 $p_{3/2}$ XPS of DDG biochars, and diffraction evidence for sylvite in the 900 °C HTT DDG biochar all indicate that Cl in the DDG biochars was in the form of sylvite.

A closer look (5000x magnification) at BC-ZVI produced from switchgrass at the HTT of 900 °C reveals that surface Fe in this biochar was in the form of oxides (Fig. 4.4).
Fig. 4.3: SEM micrographs and elemental maps of Fe, Si, and Cl for fresh BC-ZVI produced by pyrolysis at 900 °C HTT of the following FeCl₃ treated feedstock; (a) switchgrass, (b) corn stover, (c) red oak, and (d) cellulose.
Figure 4.4: High resolution SEM-EDS analysis (5000x magnification) of fresh BC-ZVI produced from pyrolysis of switchgrass at 900 °C HTT.

### 4.3.6 Suitable feedstocks for ZVI production

A positive correlation between Fe and Si and a negative correlation with Cl is observed at closer magnification. The EDS spectra compare composition of an Fe-rich phase in the left of the micrograph to an Fe-poor region closer to the middle. The diffuse background of Cl evidenced in the SEM-EDS analysis (Figs. 4.3, 4.4) and XRD evidence for sylvite (Fig. 4.1) indicate dispersion of nanometer-scale sylvite crystallites scattered throughout
the biochar. Likewise, the concomitant presence of Si and absence of Fe in portions of the elemental maps and poor correlation of these elements in the EDS spectra illustrate different phases with different compositions and are consistent with the combined quartz, sylvite, fayalite, and ZVI crystalline phases identified by XRD in this biochar. The small size of ZVI phases in this biochar and dispersion of Fe among other elements facilitated rapid oxidation of ZVI. For purposes of environmental application, BC-ZVI composites produced from switchgrass, corn stover, or other high Si feedstocks would experience rapid oxidation of ZVI during storage and handling, rendering the product less useful. However, BC-ZVI complexes produced from red oak and other lignocellulosic feedstocks with low Si content are potentially more suitable for environmental applications as ZVI produced from such materials and Fe oxides corrodes at a lower rate.

4.4 Acknowledgements

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References
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APPENDIX C. SUPPORTING INFORMATION FOR CHAPTER 4

Figure S4.1 XRD patterns of fresh and aged BC-ZVI produced from cellulose. M = Magnetite, Z = ZVI.

Figure S4.2 XRD patterns of fresh and aged BC-ZVI produced from corn stover. F = Fayalite, M = Magnetite, Q = Quartz, S = Sylvite.
Figure S4.3  XRD patterns of fresh and aged BC-ZVI produced from DDG. S = Sylvite, B = Barringerite, Sc = Schreibersite, K = K$_2$Fe$_2$P$_8$O$_{24}$.

Figure S4.4  XRD patterns of fresh and aged BC-ZVI produced from red oak. C = CaO, M = Magnetite, Q = Quartz, S = Sylvite, Z = ZVI.
Figure S4.5 XRD patterns of fresh and aged BC-ZVI produced from switch grass. F = Fayalite, M = Magnetite, S = Sylvite, Q = Quartz, Z = ZVI.

Figure S4.6 XRD patterns of 110 ZVI reflection of fresh biochars.
Table S4.1 Chemical analysis of biochars. Values reported as mass percent.

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CHAPTER 5.
MACROPOROUS CARBON SUPPORTED ZEROVALENT IRON FOR REMEDIATION OF TRICHLOROETHYLENE

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Michael Lawrinenko, a Zhuangji Wang, a Robert Horton, a Deyny Mendivelso-Perez, b Emily A. Smith, b Terry E. Webster, c David A. Laird a, and J. (Hans) van Leeuwen d*

a Department of Agronomy, Iowa State University, Ames, IA.
b The Ames Laboratory, U.S. Department of Energy, and Department of Chemistry, Iowa State University, Ames, IA.
c Des Moines Water Works, Des Moines, IA.
d Departments: Civil, Construction & Environmental Engineering; Ag & Biosystems Engineering; Food Science & Human Nutrition, Iowa State University, Ames, IA.

*corresponding author: leeuwen@iastate.edu

Abstract

Groundwater contamination with chlorinated hydrocarbons has become a widespread problem that threatens water quality and human health. Permeable reactive barriers (PRBs) which employ zerovalent iron are effective for remediation, however a need exists to reduce the economic and environmental costs associated with constructing PRBs. We present a method to produce zerovalent iron supported on macroporous carbon using only lignin and magnetite. Biochar-ZVI (BC-ZVI) produced by this method exhibits a broad pore size distribution with micrometer sized ZVI phases dispersed throughout a carbon matrix. X-ray diffraction revealed that pyrolysis at 900°C of a 50/50 lignin-magnetite mixture resulted in almost complete reduction of magnetite to ZVI and that compression molding promotes iron reduction in pyrolysis due to mixing of starting materials. High temperature
pyrolysis of lignin yields some graphite in BC-ZVI due to reduction of carbonaceous gases on iron oxides. TCE was removed from water as it passed through a column packed with BC-ZVI at flow rates representative of average and high groundwater flow. One-dimensional convection-dispersion modeling revealed that adsorption by biochar influences TCE transport and that BC-ZVI facilitated removal of TCE from contaminated water by both adsorption and degradation.

5.1 Introduction

Permeable reactive barriers (PRBs) have been widely used to remediate groundwater contaminated with chlorinated hydrocarbons.\(^1\,2\) Zerovalent iron (ZVI) is most commonly employed in PRBs as an electron source to reductively dechlorinate the parent molecule to residual hydrocarbon and chloride. While effective, PRBs are costly because of expensive raw materials. Poor adsorption affinity and low contaminant solution concentrations limit the kinetics of remediation, particularly affecting performance during high groundwater velocities. Expected service lives of PRBs was originally estimated at around 25 years, however a recent lifecycle analysis reported that most PRBs only operate for about 10 years. This is due to declining reactivity of the permeable barrier material and declining hydraulic conductivity due to illuvial deposition of soil materials.\(^1\) These challenges call for a need to improve reactive barrier material to increase reliability and service life. Improved PRB material and construction methods would have positive impacts on the economics and performance of this technology. Further, alternate PRB media with lower global warming impact would more comprehensively benefit the environment than material produced by conventional
means. Ideally, new technologies designed to produce PRB media with improved reliability and performance characteristics should also employ production practices that consume less energy and emit less greenhouse gases than current manufacturing processes.

Various approaches to improving reaction kinetics of PRB media have recently been reported: co-mixing activated carbon (AC) with ZVI, catalyst enhanced ZVI such as palladized ZVI, and development of biochar-ZVI (BC-ZVI) and AC-ZVI composites. Both BC-ZVI and AC-ZVI composites demonstrate increased degradation kinetics of TCE over ZVI, due to adsorption of the contaminant on the C phase. Despite promising performance reports, the high costs of activated carbon, binding agents, and rare-earth metals render options that employ these materials cost-prohibitive. Furthermore, leaching of certain catalyst metals poses other environmental risks; adding to the incumbent problem of the contaminant. All of these approaches lead to materials designed to be mixed with sand, as PRBs have been traditionally constructed, offering no solution to prevent pore clogging and decreasing hydraulic conductivity caused by soil illuviation. Production of reactive media reported in most of these studies employed borohydride reduction which is also costly, energy intensive, and offers no way to reduce the climate impact of ZVI production.

Pyrolysis of biomass pretreated with iron salts has been demonstrated to produce ZVI. In pyrolysis, organic materials are heated under low oxygen conditions, thermally transforming the organic material into charcoal, also known as biochar, while oxidized iron is simultaneously reduced to ZVI and other crystalline forms of iron. Biochar
production can be C neutral as the amount of atmospheric C sequestered in soil may equate to C released from fossil fuel utilized for harvesting and processing of biomass.\textsuperscript{15,16} The carbon sequestered in soil with biochar application and replacement of fossil fuel with biorenewable C to produce ZVI both reduce carbon dioxide released to the atmosphere, thus lowering the climate impact associated with the manufacture of PRB material.\textsuperscript{3} Previous work revealed that pyrolysis at 700 °C and 900 °C of various biomass feedstocks pretreated with FeCl\textsubscript{3} yielded biochars containing significant amounts of reduced Fe as magnetite and ZVI, respectively; however feedstock chemistry and pyrolysis temperature influenced the reduction of iron.\textsuperscript{14} Pyrolysis based production of ZVI is potentially beneficial to the environment and more cost-effective than current production methods as biorenewable organic materials and low-cost iron oxides can be used for feedstocks.

Permeable reactive barriers require hydraulic conductivities greater than that of surrounding soil in order to perform. Pyrolysis-based ZVI previously reported\textsuperscript{8,10,14} were small particulates which would be subject to eluviation and displacement in a PRB. One way to possibly overcome this challenge is to produce large particle BC-ZVI for use as media in PRBs. This innovation would eliminate the need for sand matrices in PRB construction. Biochars produced from most biomass feedstocks resemble precursor materials by size and shape characteristics. Even the anatomical structure of plant materials is preserved.\textsuperscript{17} Frangibility and low crushing strength of charcoals and biochar contribute to rapid physical deterioration in production and handling, thus even sizing of feedstock could only produce an ideal biochar size fraction of limited yield. For this reason, granular activated carbons cost several times more than powders. Producing large
particle size biochar is thus challenging and processes that utilize whole plant materials could at best be optimized with low yield to produce large particle BC-ZVI.

We sought to address the need for low-cost but effective PRB media with a relatively small climate impact, by producing biochars from mixtures of lignin and magnetite. Lignin is an abundant and low-cost plant biopolymer that is available as a byproduct from paper pulp processing, sugarcane processing, and second generation ethanol production; lignin is biorenewable, and is often burned for process heat or landfilled. Magnetite (Fe₃O₄) is abundantly available as an iron ore and can be obtained at low-cost in bulk quantities in a powdered form. We hypothesized that pyrolysis of mixtures of lignin and powdered magnetite would yield BC-ZVI materials that possess appropriate physical and chemical properties for PRB use.

5.2 Materials and Methods

5.2.1 Biochar Preparation

Biochars were prepared by slow pyrolysis of lignin (control biochar) or lignin-magnetite mixtures in a stainless steel box contained in a muffle furnace and heated from ambient temperature to 900 °C over four hours. During pyrolysis and throughout cool-down, samples were purged under 200 mL min⁻¹ N₂ gas. Lignin was supplied by Archer Daniels Midland Corporation. This lignin was a co-product of their Acetosolv process, a modified organosolv process, which is used to extract cellulose from corn stover for fuel-ethanol production. Magnetite was ore grade powder obtained from the Division of Lands & Minerals, Minnesota Department of Natural Resources and was dried in a convection oven prior to use. Lignin was ground in a mortar and pestle. Lignin and magnetite mixtures of 50/50 or 30/70
gravimetric ratios were mixed in a beaker and immediately pyrolyzed (unpressed sample). Pressed samples were prepared by compression molding of lignin-magnetite mixtures in a 4 inch ID cylindrical aluminium compression mold preheated to 180 °C under 20 tonne pressure (about 239 MPa), after which the resulting pellet was pyrolyzed (pressed samples). Resulting biochars were diced on a cutting board and screened between #4 and #12 screens (1.68 to 4.76 mm). This granule fraction was utilized for all analyses.

5.2.2 X-ray Diffraction (XRD) Analysis

Diffraction patterns of biochar samples were collected from 10 to 90° 2θ with a Siemens D5000 x-ray diffractometer using Cu Kα 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 s per step. Fixed 1.0° divergence and 3.0° anti-scattering slits were used with a scintillation counter. Random powder mounts of biochars ground in an agate mortar were analyzed at ambient temperature and humidity. The XRD patterns were analyzed using JADE v9.0.

5.2.3 Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDS) Analysis

Microscopy 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. Elemental maps were obtained by energy dispersive x-ray analysis using an Oxford Aztec EDS. Granular samples were mounted to the top of a 12.5 mm carbon stub using double-sided graphite tape by compressing the taped stub against a subsample of biochar. For elemental analysis, 1 g samples of biochar were ground in an agate mortar,
transferred to a sample cup, and dosed with several drops of hexane which was used to extract adhesive from tape. The adhesive was necessary to hold biochar particles in place to avoid microscope contamination. With volatilization of hexane, the small amount of C added to the samples by the adhesive likely did not alter the bulk sample composition. Elemental analysis was performed by averaging triplicate EDS spot analyses. Thermal combustion analysis using an Elementar Vario Micro Cube was also performed to more accurately determine C, H, N, and S contents.

5.2.4 Raman Spectroscopy

Raman measurements were performed at ambient temperature using an XploRa Plus confocal Raman microscope (Horiba Scientific/JY, France) equipped with a 532-nm laser excitation source, operated at 25mW. An objective with a 0.9 numerical aperture (Olympus, Melville, NY) was used to collect the Raman signal. Biochars were ground in a ball mill for 2 minutes to a fine powder. Graphite standards (UCAR SP-1, Graphite Standard I, Lot# B74, Union Carbide; Sigma-Aldrich synthetic graphite, Graphite Standard II, Lot# 08017EH) were analyzed as received. Approximately 20 mg of sample was pressed onto a glass slide forming a dense layer about 1mm thick, and placed on the microscope sample holder for analysis. This was repeated 6 times for each sample. Reported spectra were averaged from 6 subsamples acquired in triplicate, for a total of 18 spectra, with a 10s acquisition time for each spectrum.

5.2.5 Miscible-Displacement Experiment

Breakthrough curves of aqueous TCE were measured using stainless steel 22 mm ID x 100 mm columns (Alltech) packed with biochar granules using a modified influent pulse method described by Casey et al. (2000). The pressed 50/50 BC-ZVI and the biochar
control materials were used for this study. Two flow rates were employed, representative of high (12.2 mm min\(^{-1}\)) and average (5.6 mm min\(^{-1}\)) groundwater pore water velocities.\(^{18}\) These flow rates are reported as “fast” and “slow” in the results. Milli-Q water was used for preparation of TCE (>99% Alfa-Aesar, Lot# X17A014) solutions and breakthrough curve measurements. Water was delivered by peristaltic pump and one-pore volume of pulses ~50 mg L\(^{-1}\) TCE were injected by a programmable syringe pump equipped with a stainless steel syringe (Cole Parmer). Assay of pulse samples taken prior to and after pulse was averaged to determine influent TCE concentration. Both pumps were calibrated to deliver equal flow rates. Columns were initially purged with five pore volumes of water to thoroughly displace air from biochar prior to breakthrough curve measurements. Particle density of biochars was measured by helium pycnometry and bulk density was determined from the mass of biochar contained in the columns. Column effluent was passed through stainless steel tubing and sequential samples were collected in 1.2 mL gas chromatographic (GC) sample vials and immediately sealed without headspace using vial caps equipped with Teflon seals. Aliquots were withdrawn from these sample vials and diluted into 40 mL glass vials containing about 35 mL water, 250 mg ascorbic acid, and six drops of 50% HCl, filled with water to eliminate headspace, and capped with plastic caps equipped with pierceable Teflon septa. TCE and degradation byproducts were assayed in accordance with EPA Method 524.2\(^{19}\) using a purge and trap GC (Varian CP 3800) equipped with a Tekmar Dorhmann 25 mL purge vessel, Varian Saturn 2200 mass spectrometer, and Restek RTX VMS 60 m x 0.32, 0.32 mm ID GC column. Restek 502.2 Cal 200 Mega Mix, 502.2 Calibration Mix 1, and 524 Internal Standard Surrogate Mix were used for calibration. Data were processed using a Saturn GC/MS workstation v5.52.
5.2.6 Mathematical Model

A convection-dispersion chemical transport model was fitted to the measured column effluent breakthrough curve data. CXTFIT v2.1\(^{20}\) was used to estimate the retardation factor \((R)\) and combined first order adsorption / degradation rate coefficient \((\mu)\). In this model, \(R\) implies the empirical distribution of TCE between the adsorbed and liquid phases. Since BC-ZVI adsorbs and actively degrades TCE, an empirically regressed coefficient \(\mu\) is chosen to represent the efficiency of TCE reduction in comparing BC-ZVI to control biochar. Therefore, the measured TCE breakthrough curves at two flow rates for BC-ZVI and control were fitted with the convection-dispersion equation (CDE) for one dimensional transport of TCE, subject to equilibrium adsorption and first-order degradation kinetics:

\[
R \frac{\partial c_r}{\partial t} = D \frac{\partial^2 c_r}{\partial z^2} - v \frac{\partial c_r}{\partial z} - \mu c_r
\]  

(1)

where \(c_r\) is the resident concentration of TCE, \(v\) is the average pore-water velocity, \(t\) is time, \(z\) is distance from the influent end of the column, and \(D\) is the dispersion coefficient, which relates to the dispersivity \((\lambda)\) and \(v\), i.e., \(D = \lambda v\). \(R\) is given by

\[
R = 1 + \frac{\rho_b K_d}{\theta}
\]  

(2)

and \(\mu\) is given by the first order rate in the liquid, \(\mu_l\), and adsorbed phases, \(\mu_s\):

\[
\mu = \mu_l + \frac{\rho_b K_d \mu_s}{\theta}
\]  

(3)

\(\rho_b\) is the bulk density of the packed biochar granules, \(K_d\) is the distribution coefficient, and \(\theta\) is the volumetric water content. A nonlinear least-squares optimization method\(^{21}\) is used in CXTFIT to determine the optimal values of \(R\) and \(\mu\). In this model, the values of \(\lambda\) were
determined from the fast breakthrough curves and applied to fit the slow breakthrough curves for respective control and BC-ZVI treatments.

5.3 Results and Discussion

5.3.1 Biochar Characterization

Lignin and magnetite employed in this study were fairly clean raw materials, with the lignin having an ash content of 0.43% and overnight loss on drying at 105 °C and XRD analysis (not shown) of the magnetite revealed 7% moisture content and evidence of both magnetite and maghemite, though magnetite was the dominant crystalline structure detected in the sample. Elemental analysis of the resulting BC-ZVI and control biochar (pyrolyzed lignin without magnetite) presented in Table 5.1 reveal that the control biochar was well carbonized with approximately 8% O content, measured by the difference of N, C, H, S, and ash fractions determined by thermal combustion from unity, which is in good agreement with 10.47% O determined by SEM-EDS analysis. The low H content of this biochar is consistent with extensive condensed aromatic character of C. Though the 30/70 lignin-magnetite mixtures were prepared and pyrolyzed under the same conditions, lower C yield is observed in BC-ZVI produced from unpressed materials, suggesting that compression molding causes higher char yield. More production replicates would be necessary to better understand the effect of compression molding on C yield. The N, C, H, and S contents determined by thermal combustion are more veritable than determined by SEM-EDS analysis, because of better representative sampling and the fact that particle settling in the sample cup used in the EDS analysis can cause bias as lighter particles can redistribute to the top of the sample during preparation. The major elements detected in
these biochars by EDS are C, O, and K likely as K₂O due to the lack of other anions, and additionally Fe for BC-ZVI.

Table 5.1: Elemental analysis of BC-ZVI and lignin control biochar.

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<td>2.36</td>
<td>0.14</td>
</tr>
<tr>
<td>S</td>
<td>0.14</td>
<td>0.07</td>
<td>0.18</td>
<td>0.16</td>
</tr>
<tr>
<td>K</td>
<td>0.52</td>
<td>0.22</td>
<td>0.18</td>
<td>2.92</td>
</tr>
<tr>
<td>Ca</td>
<td>0.66</td>
<td>0.55</td>
<td>0.89</td>
<td>0.13</td>
</tr>
<tr>
<td>Fe</td>
<td>31.07</td>
<td>36.95</td>
<td>44.86</td>
<td>0.06</td>
</tr>
</tbody>
</table>

aData from thermal combustion. bData from SEM-EDS analysis.

Scanning electron microscopy revealed a broad pore size distribution in both control biochar and BC-ZVI ranging from microns to several millimeters (Fig. 5.1). Large pores promote hydraulic conductivity and are necessary for PRBs to function effectively. Some pores observed in BC-ZVI may be continuous and allow for intraparticle transport, but interparticle pore size can be designed by particle sizing. Thus, BC-ZVI production using lignin and magnetite could be employed to create any size fraction or desired shape of the product material. Iron phases, indicated by lighter regions in the 5000x micrographs of BC-ZVI, ranged from nanometers to several microns in size. No differences were observed in the distribution or size of Fe phases in BC-ZVI produced from different feedstock ratios. Iron phases in BC-ZVI were separated by regions of C, suspended by the solid foam matrix of biochar C. This physical structure was owed to the physical properties of the particular lignin selected for this study which flowed under pressure. Gas expansion during pyrolysis
expanded lignin as it pyrolyzed, resulting in a solid porous foam. We evaluated several sources of lignin for this study, however, only the ADM lignin yielded the desired physical structure of BC-ZVI upon pyrolysis; water soluble lignins yielded powder biochars (unreported data from this study). The lignin employed to produce biochars for this study was water and hexane insoluble material of frangible nugget consistency which exhibited decreased viscosity upon heating. Plasticity of lignin was crucial to successful melt processing as the lignin was used to suspend magnetite particles in a thermoplastic matrix which transformed to char and gases upon pyrolysis.

Fig. 5.1: SEM micrographs of pressed BC-ZVI and control biochar. Lighter regions in the 5000x micrographs are Fe phases.
XRD patterns of BC-ZVI and control biochar produced from lignin are depicted in Fig. 5.2. D-spacings and relative intensities for XRD peaks of mineral phases detected in the biochars are provided in Table 5.2 to facilitate interpretation of the diffraction patterns. Thermal transformation of lignin and magnetite mixtures heated to 900 °C yielded biochar compositied with ZVI and residual magnetite and wüstite. Silicon in lignin transformed to quartz with pyrolysis. Evidence for wüstite was observed in XRD patterns of biochars prepared from the 30/70 lignin-magnetite mixtures. The relative intensity of wüstite to α-Fe (ZVI) and magnetite peaks was greater for BC-ZVI produced from the pressed versus the unpressed mixture. Phase transformation of magnetite to ZVI during pyrolysis was a reduction process that proceeded through an intermediate wüstite phase at high temperature and low oxygen fugacity. Wüstite was a metastable phase that eventually decomposed to ZVI and magnetite after cooling. Greater relative intensities of wüstite reflections observed in the XRD pattern of 30/70 pressed biochar indicated that more Fe was in this phase after pyrolysis, illustrating an effect of compression molding on Fe transformation. Compression molding caused better mixing of lignin and magnetite particles during the melt processing step and facilitated more Fe conversion to wüstite. No evidence for wüstite was observed in BC-ZVI produced from the 50/50 mixture, with greater relative intensities of α-Fe to magnetite reflections indicating more transformation of magnetite to ZVI in this mixture. While residual magnetite was observed in all BC-ZVI, the 50/50 mixture yielded the most reduction of Fe to ZVI. This greater reduction of Fe observed in the 50/50 mixture was due to reduction by solid C and reducing gases produced at high pyrolysis temperatures, however observed residual magnetite
suggested that the ratio of feedstock materials could be optimized by greater lignin content and that longer heating times would allow more wüstite conversion to ZVI.

The control biochar (c) exhibited a diffraction pattern typical of biochar, with broad amorphous carbon reflections centered at 22, 44, and 80 \(^\circ\)2\(\Theta\). While C in these biochars was dominantly amorphous, evidence for graphite was observed in BC-ZVI, with greater intensity observed in the BC-ZVI produced from 50/50 lignin-magnetite.

Fig. 5.2: XRD patterns of BC-ZVI produced from lignin and magnetite and control biochar produced from lignin. Letter identifiers describe feedstock preparation: a = 50% lignin / 50% magnetite (pressed), b = 30% lignin / 70% magnetite (pressed), c = control biochar from lignin, d = 30% lignin / 70% magnetite (unpressed). Peak labels represent crystalline structures found in biochar: \(\alpha\)-Fe = Zerovalent iron, G = graphite, M = Magnetite, Q = Quartz, W = Wüstite.
Table 5.2: d-spacing (d) and relative intensity (I) for XRD peaks of mineral phases found in the biochars (JADE v9.0).

<table>
<thead>
<tr>
<th>Mineral Phase</th>
<th>° 2Θ</th>
<th>d(Å)</th>
<th>I(f)</th>
<th>° 2Θ</th>
<th>d(Å)</th>
<th>I(f)</th>
<th>° 2Θ</th>
<th>d(Å)</th>
<th>I(f)</th>
<th>° 2Θ</th>
<th>d(Å)</th>
<th>I(f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>26.5</td>
<td>3.36</td>
<td>100</td>
<td>20.86</td>
<td>3.255</td>
<td>100</td>
<td>44.67</td>
<td>2.027</td>
<td>100</td>
<td>36.26</td>
<td>2.475</td>
<td>50</td>
</tr>
<tr>
<td>Quartz</td>
<td>44.6</td>
<td>2.03</td>
<td>50</td>
<td>26.64</td>
<td>3.343</td>
<td>100</td>
<td>35.42</td>
<td>2.532</td>
<td>100</td>
<td>65.03</td>
<td>1.433</td>
<td>20</td>
</tr>
<tr>
<td>Magnetite</td>
<td>54.6</td>
<td>1.67</td>
<td>80</td>
<td>36.54</td>
<td>2.457</td>
<td>10</td>
<td>43.06</td>
<td>2.099</td>
<td>20</td>
<td>82.35</td>
<td>1.17</td>
<td>30</td>
</tr>
<tr>
<td>ZVI (α-Fe)</td>
<td>77.4</td>
<td>1.23</td>
<td>30</td>
<td>39.47</td>
<td>2.281</td>
<td>10</td>
<td>53.38</td>
<td>1.715</td>
<td>10</td>
<td>99.01</td>
<td>1.013</td>
<td>10</td>
</tr>
<tr>
<td>Wüstite</td>
<td>83.39</td>
<td>1.15</td>
<td>50</td>
<td>42.44</td>
<td>2.128</td>
<td>10</td>
<td>56.93</td>
<td>1.616</td>
<td>30</td>
<td>116.5</td>
<td>0.906</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>86.9</td>
<td>0.99</td>
<td>40</td>
<td>50.13</td>
<td>1.818</td>
<td>10</td>
<td>62.53</td>
<td>1.484</td>
<td>40</td>
<td>137.1</td>
<td>0.8275</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>101</td>
<td>0.99</td>
<td>40</td>
<td>59.98</td>
<td>1.541</td>
<td>10</td>
<td>73.92</td>
<td>1.281</td>
<td>10</td>
<td>73.01</td>
<td>1.237</td>
<td>20</td>
</tr>
</tbody>
</table>

Raman spectroscopy was performed on biochars to obtain information regarding the structure of carbon in these materials. All data were processed using Igor Pro 6.37 scientific analysis and graphing software (Wavemetrics, Lake Oswego, OR, USA). Spectra were fitted to a Gaussian function with a linear baseline using the multi-fit peak function in order to extract peak intensity (height) and center position (Table 5.3). Graphitic material exhibits characteristic Raman bands around 1580 cm⁻¹ (E₂g, G band) and 1360 cm⁻¹ (A₁g, D band). The D band is attributed to the presence of structural defects. The intensity ratio $I_D/I_G$ between the D and G band has been widely used as a measure of defects in graphite-based materials. The overtone of the D band around 2700 cm⁻¹ (2D or G') is measured in highly ordered graphitic material.

Fig. 5.2 shows the Raman spectra of two graphite standards, lignin control biochar, and BC-ZVI produced from feedstock with different lignin/magnetite ratios. The D band and G band are present in the Raman spectra of the biochar materials, illustrating the graphitic character of the samples. However, the biochar samples present broader G and D bands compared to the highly ordered graphite standards, which indicates a more highly disordered structure in the biochar samples. The $I_D/I_G$ intensity ratios provided in Table 5.3 also reveal a more highly disordered graphitic character of C in the BC-ZVI and control
biochar, with the graphite standards exhibiting one to two orders of magnitude lower $I_D/I_G$ ratios compared to the spectra of biochars. $I_D/I_G$ ratios in BC-ZVI at different lignin/magnetite ratios are statistically greater ($p = 0.0266$) than the lignin control biochar, suggesting that the presence of magnetite during the pyrolysis of lignin induces some level of disorder within the biochar structure, giving C in BC-ZVI samples a greater level of disorder than detected in control biochar.

Graphitic reflections observed in the XRD patterns of BC-ZVI (Fig. 5.2) indicate crystalline character of graphite in BC-ZVI. This difference between graphitic C in BC-ZVI and the control was likely caused by better crystalline ordering of C that deposited as graphite on wüstite and magnetite surfaces by the reduction of carbonaceous pyrolysis gases at high temperatures. Thus, graphite in these biochars formed by two mechanisms: graphitization of lignin in pyrolysis and reduction of carbonaceous gases on Fe oxide surfaces; the latter contributing to increased graphite content in BC-ZVI versus control.
Fig. 5.3: Raman spectra of graphite standards, lignin control biochar, and BC-ZVI.

Table 5.3: Raman shifts of D and G bands of graphite standards, lignin control biochar, and BC-ZVI. D/G height ratio reported as mean ± standard deviation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D Band</th>
<th>G Band</th>
<th>D/G Height Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite Standard I</td>
<td>1335 cm⁻¹</td>
<td>1562 cm⁻¹</td>
<td>0.013 ± 0.002</td>
</tr>
<tr>
<td>Graphite Standard II</td>
<td>1326 cm⁻¹</td>
<td>1554 cm⁻¹</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>Lignin Control Biochar</td>
<td>1330 cm⁻¹</td>
<td>1573 cm⁻¹</td>
<td>1.18 ± 0.02</td>
</tr>
<tr>
<td>Unpressed 30/70 BC-ZVI</td>
<td>1321 cm⁻¹</td>
<td>1566 cm⁻¹</td>
<td>1.29 ± 0.03</td>
</tr>
<tr>
<td>Pressed 50/50 BC-ZVI</td>
<td>1324 cm⁻¹</td>
<td>1563 cm⁻¹</td>
<td>1.28 ± 0.03</td>
</tr>
<tr>
<td>Pressed 30/70 BC-ZVI</td>
<td>1324 cm⁻¹</td>
<td>1568 cm⁻¹</td>
<td>1.21 ± 0.02</td>
</tr>
</tbody>
</table>

5.3.2 Degradation of TCE by BC-ZVI

Characterization results indicate that the 50/50 lignin-magnetite feedstock produced macroporous biochar with zerovalent iron phases dispersed throughout the material.
Breakthrough curves of TCE through a column packed with BC-ZVI and control biochar were used to evaluate interactions between BC-ZVI and a model chlorinated hydrocarbon, TCE. The relative concentration maxima in the breakthrough curves of BC-ZVI (Fig. 5.4) were significantly smaller than the relative concentration maxima of the control. Compared to the control biochars, substantially less TCE transported through the BC-ZVI material, with 96% and 99% removal achieved at the fast and slow flow rates. As BC-ZVI has little C relative to the control biochar (Table 5.1), we can deduce that degradation rather than adsorption is the main cause for the low relative concentrations in the BC-ZVI breakthrough curves. The relative TCE concentrations in the fast-flow breakthrough curve are larger than those in the slow-flow breakthrough curve for both control and BC-ZVI treatments. Fast flow rates reduce the available time for TCE to interact with the biochar granules, which limits adsorption and degradation. At slower flow rates, TCE transport has a larger diffusion component which promotes adsorption and degradation.

The equilibrium adsorption model was fitted to the control and BC-ZVI breakthrough curves under slow and fast flow rates. The regression coefficients of determination ($r^2$) were all greater than 0.95. Values for $\mu$ (Fig. 5.4) of BC-ZVI were significantly larger than those of control biochar for fast ($p < 0.0001$) and slow ($p < 0.0001$) flow rates, indicating that TCE removal from water by BC-ZVI is largely due to degradation. Though degradation dominantly accounts for the value of this coefficient in breakthrough curves of BC-ZVI, significant differences in values of $\mu$ ($p = 0.0309$) are associated with flow rate, indicating the need to design PRB width based on expected groundwater flow rates. Values of $\mu$ for control biochars were not significantly different ($p = 0.0502$), indicating that adsorption of TCE to biochar also influences transport. Consistent with kinetics
adsorption of TCE to biochar may promote degradation by increasing its local concentration near reactive iron surfaces. Trace concentrations of ethylene chloride and chloroethane were detected in BC-ZVI effluent samples, while no evidence of TCE degradation products was observed with control measurements. The presence of these degradation products indicated that TCE reacted with ZVI, however mass recovery was not possible due to volatilization losses during sampling. These results indicate that biochar C contributes to adsorption of TCE and when composites with ZVI, together can effectively remediate water contaminated with TCE.

<table>
<thead>
<tr>
<th>Label</th>
<th>Treatment</th>
<th>λ</th>
<th>v</th>
<th>D</th>
<th>R</th>
<th>μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-ZVI Fast</td>
<td>58</td>
<td>12.1</td>
<td>700</td>
<td>1.94(±0.12)</td>
<td>4.85(±0.18)</td>
<td></td>
</tr>
<tr>
<td>BC-ZVI Slow</td>
<td>58</td>
<td>5.6</td>
<td>320</td>
<td>2.20(±0.2)</td>
<td>8.86(±0.37)</td>
<td></td>
</tr>
<tr>
<td>Control Fast</td>
<td>7</td>
<td>12.2</td>
<td>90</td>
<td>0.98(±0.02)</td>
<td>0.18(±0.03)</td>
<td></td>
</tr>
<tr>
<td>Control Slow</td>
<td>7</td>
<td>5.7</td>
<td>40</td>
<td>1.02(±0.03)</td>
<td>0.53(±0.05)</td>
<td></td>
</tr>
</tbody>
</table>

Values reported as mean (± half of confidence interval); λ(mm): dispersivity; v(mm min⁻¹): mean pore liquid velocity; D(mm² min⁻¹): dispersion coefficient; R: retardation factor; μ(min⁻¹): first order adsorption/degradation rate;

**Fig. 5.4: TCE Breakthrough curves of control and BC-ZVI and model parameters.**
5.3.3 Environmental Implications

BC-ZVI produced in this study can effectively degrade aqueous TCE. Particle size may have to be adjusted to increase diffusion in order to optimize TCE removal from water, which could be easily adapted by cutting and sizing or even extrusion. Some potential applications are use of BC-ZVI as a media in PRB and as a granular reactive carbon material for pump and treat applications. The particle density of the 50/50 BC-ZVI is 5.67 g mL\(^{-1}\), thus this material would not be subject to floating. PRBs are generally constructed with ZVI mixed with sand. One major cause for decreased PRB service life using this construction approach is pore-clogging by the deposition of clay and silt.\(^1\) Elimination of sand from PRB construction would reduce the global warming impact of PRB construction methods associated with mining, processing, and transportation. Large (3 mm) intraparticle pore diameters observed in BC-ZVI produced in this study and the fact that BC-ZVI could potentially be sized in production indicate that BC-ZVI could be designed to exhibit greater saturated hydraulic conductivities than sand-ZVI mixes, thus would be resistant to soil deposition within the PRB, extending service life, and eliminating the need for a sand matrix. For these reasons, column experiments were performed using only packed granules to reveal how BC-ZVI without sand would perform as a PRB. Further research is needed to assess this BC-ZVI as a PRB to understand 3-dimensional spacial and time dependent transport of chlorinated hydrocarbon contaminants and to evaluate service life of PRB constructed entirely of BC-ZVI.

5.4 Conclusions

Macroporous carbon supported ZVI was successfully produced by pyrolysis of lignin and magnetite at 900 °C. A 50/50 mixture of these materials yielded almost complete
reduction of magnetite to ZVI. Compression molding promoted iron reduction due to mixing of feedstock materials achieved with melt processing. Residual magnetite and wüstite in fresh BC-ZVI suggested that longer pyrolysis times and greater lignin ratio could optimize iron reduction. Pyrolysis of lignin yielded carbon in control biochar and BC-ZVI that was both amorphous arene C and disordered graphite. Pulse breakthrough curves revealed that adsorption and degradation of TCE both influenced transport of this contaminant and that BC-ZVI produced from lignin and magnetite successfully degraded TCE. Further testing of space and time scales should be performed to evaluate use of this BC-ZVI as a PRB.

5.5 Acknowledgements

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References


CHAPTER 6. CONCLUSIONS

Pyrolysis can be used to produce biochars with specific properties. Diverse biomass feedstocks were explored in this research; namely alfalfa meal, cellulose, corn stover, dry distiller’s grain, lignin, red oak, and switchgrass. Though feedstocks vary in composition, biochar resulting from the pyrolysis of different biomass materials possess similarities in surface chemistry. Pyrolysis temperature is the most influential process variable, which controls surface chemistry and the transformations of feedstock elements. Pyrolysis can be employed for making green and sustainable products such as anion adsorbents and zerovalent iron for environmental remediation. These advances can be used to increase the value of biochar in support of pyrolysis based bioenergy production by renewing waste materials to useful products.

Anion Exchange

Anion exchange capacity (AEC), detected in biochars produced from several feedstocks, was greater in biochars produced at 700 °C than 500 °C and decreased with increasing pH. Greater AEC observed at the higher pyrolysis temperature is due to the formation of oxonium (O+) heterocycles and greater condensed aromatic character of biochar carbon. Oxonium heterocycles have positive formal charge, thus contribute pH independent positive surface charge to biochar. By contrast, condensed aromatic carbon provides pH dependent surface charge under acidic conditions by stabilizing protons in the π aromatic ring system. Other basic sites, particularly pyridinium moieties may also impart positive surface charge to biochars when protonated.

These sources of AEC, attributed to the organic surface chemistry of biochar, declined after 4 months of alkaline ageing treatments. Biochars produced at 700 °C exhibited higher
AEC that was partially recalcitrant to ageing treatments compared to biochars produced at 500 °C. Decline in AEC during ageing is partly attributed to the reduction of O⁺ heterocycles to pyran structures due to nucleophilic attack on non-bridging α-C by hydroxide. Oxonium atoms bonded to two bridging aromatic C atoms are sterically resistant to nucleophilic attack, thus contribute persistent pH-independent AEC. Carbon in biochars produced at 700 °C has more condensed aromatic character than in biochars produced at 500 °C therefore was more likely to have O⁺ atoms with two adjacent bridging aromatic C atoms and hence AEC recalcitrant to ageing. Other possible mechanisms for the observed loss of biochar AEC during the ageing treatments include the loss of heterocyclic N in pyridinium structures and a decrease in the number of aromatic sites which may abstract protons. Both of these processes, however, are highly pH dependent and believed to contribute little to biochar AEC at pH 6. The condensed aromatic character of biochars produced at 700 °C changed by a concerted 4 plus 2 π electron mechanism yielding endoperoxide surface structures. By contrast, the 500 °C biochars dominantly oxidized by a 2 plus 2 π electron pathway, which led to the formation of carbonyl and hydroxyl groups on surfaces of these biochars.

Aluminum and iron surface enhancements increased biochar AEC at pH 8 via metal oxyhydroxide surface coatings, which express higher points of zero net charge (PZNC) than that of control biochars. Pyrolysis of AlCl₃ pretreated biomass yielded amorphous alumina which functionalized biochar C by Al-O-C organometallic bonding structures. Pyrolysis at 700 °C yielded more functionalization than at 500 °C. Consequently, AEC was higher in biochars produced at 700 °C, partly due to increased oxonium heterocycle content, and more so due to dispersion of Al oxyhydroxides on biochar surfaces which
exhibit high PZNCs. Dispersion of Al on biochar surfaces was due to covalent bonding of Al to biochar C. Biomass pretreatment by FeCl$_3$ yielded some functionalization of biochar, however iron mostly developed crystalline forms and produced mixed effects on AEC due to the PZNC of iron mineralogies; magnetite and maghemite which formed during pyrolysis. Feedstock composition influenced the reduction of iron during pyrolysis, ranging from zero to trivalent iron in biochar produced from alfalfa meal. The AEC of biochar produced from corn stover was not significantly increased by metal oxyhydroxide functionalization, however, different biomass pretreatment rates could yield different results. While metal oxyhydroxides in biochar do contribute pH-dependent surface charges, AEC is dependent on the charge density and Lewis properties of ionizable structures on biochar surfaces and the abundance of permanent charge sites, O$^+$ heterocycles, on biochar surfaces.

**Pyrolysis based zerovalent iron for environmental remediation**

Pyrolysis can also be used to produce zerovalent iron for environmental use; specifically, the remediation of chlorinated hydrocarbons. One-step pyrolysis of various FeCl$_3$ treated biomasses yielded biochar-zerovalent iron (BC-ZVI) composites. Pyrolysis at 900 °C effectively reduced Fe$^{3+}$ to ZVI, however, P and Si in feedstock materials yielded Fe phosphides and fayalite, decreasing the yield and size of ZVI phases in BC-ZVI. Dispersion of ZVI phases and association with fayalite led to rapid oxidation of ZVI in BC-ZVI composites derived from corn stover and switchgrass. Feedstocks low in P and Si such as cellulose and red oak yielded larger ZVI aggregates which oxidize more slowly, hence are more suitable for the production of ZVI for environmental remediation.
Macroporous carbon supported ZVI was successfully produced by pyrolysis of lignin and magnetite at 900 °C. This BC-ZVI exhibits a broad pore-size distribution and could be produced to custom sizing. Pyrolysis of a 50/50 gravimetric mixture of lignin and magnetite at 900°C reduced almost all magnetite to ZVI after 4 h of heating under N₂ purge, however, feedstock ratio and heating time could be optimized to maximize the reduction of magnetite to ZVI. Compression molding promoted iron reduction due to good initial surface contact between the lignin matrix and magnetite phases which eliminated gaseous oxygen in feedstock preparation. Magnetite and wüstite detected in fresh BC-ZVI suggest that longer pyrolysis times and greater lignin content of the pre-mix could optimize iron reduction to ZVI. Pyrolysis of lignin yielded amorphous C in control biochar and both amorphous C and disordered graphite in BC-ZVI. Pulse breakthrough curves revealed that adsorption and degradation of TCE both influenced transport of this contaminant and that BC-ZVI produced from lignin and magnetite successfully degraded aqueous TCE.
CHAPTER 7. FUTURE WORK

Pyrolysis has been demonstrated to produce biochars with anion exchange properties, however a need exists to evaluate biochar interactions with various anions. Adsorption of nitrate, phosphate, heavy metal oxyanions, and non-adsorbable organic carbon in finished water are several potential uses for high AEC biochar. Future work should investigate adsorption phenomena of these anionic contaminants to biochar in order to make recommendations for practical applications. For soil application, it will be necessary to investigate the effect of competitive adsorbates such as soil organic matter and bicarbonate which dominate the alkalinity of some soils, particularly many soils in Iowa.

Though this work demonstrated that biochars can be produced with significant AEC, the discovery of aluminum oxide functionalization to biochar surfaces creates opportunities to further functionalize biochars with other catalyst metals or other functional groups to create biochars with tailored properties. It is therefore recommended to explore aluminum functionalized biochar as a platform for bonding other metals in the development of heterogeneous catalysts which could be particularly profitable.

Oxidation and ageing of biochar should also be explored in acidic environments to evaluate the effect of ageing in acidic soils on biochar AEC. Recent advances in nuclear magnetic resonance spectroscopy could provide more evidence for mechanisms of biochar ageing and experiments using isotope enriched (\(^{13}\)C, \(^{15}\)N, \(^{17}\)O) biochars would be necessary to conduct successful experiments. Further, the effect of ageing on organometallic structures formed in pyrolysis should also be investigated to determine the viability of metal functionalized biochar in natural environments.
Biochar-zerovalent iron production can be accomplished by high temperature slow-pyrolysis, however, it may also be possible to produce BC-ZVI via fast pyrolysis which could be a pathway to high-throughput production of ZVI for environmental use. Feedstocks other than lignin should also be investigated for the production of macroporous carbon supported zerovalent iron to develop several options for producing this material. While this material was demonstrated to remove trichloroethylene from water, there is also a need to optimize its physical and chemical characteristics: particle size, carbon to iron ratio, specific surface area, size of iron phases; all which influence reaction kinetics, contaminant breakthrough, and service life. Long-term studies, which evaluate the space and time scale performance of macroporous carbon as a permeable reactive barrier, are needed to recommend the use of this product for this purpose. Macroporous carbon supported zerovalent iron should also be evaluated for the removal of other redox-sensitive contaminants such as nitrate.

Biochars with anion exchange properties and zerovalent iron are just two types of products that can come from pyrolysis-based bioenergy production. Many other opportunities are yet to be discovered or created to produce new or improved products using biochar. These future innovations can facilitate an integrated pyrolysis-based bioenergy strategy that produces energy and a variety of co-products to provide a means for more sustainable and environmentally responsible manufacturing practices with reduced carbon footprint. Thus lifecycle and cost analyses are also needed to evaluate the potential of actually bringing these developments to application.