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**DEVELOPMENT AND EVALUATION OF POST-PRODUCTION
OXYGENATION TECHNIQUES FOR THE AUGMENTATION OF
BIOCHAR**

by

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A Dissertation Submitted to the Faculty of
Old Dominion University in Partial Fulfillment of the
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ABSTRACT

DEVELOPMENT AND EVALUATION OF POST-PRODUCTION OXYGENATION TECHNIQUES FOR THE AUGMENTATION OF BIOCHAR

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Biochar is the carbon rich solid by-product of biomass pyrolysis. Interest in biochar can be broken down to several main categories: use as a carbon sequestration agent, use as a medium for the removal via adsorption of unwanted materials in wastewater, and as a soil amendment for the increase of cation exchange capacity (CEC). In order to generate a biochar which is stable enough for carbon sequestration, higher temperature pyrolysis must be used in order to ensure a lower O:C ratio in order to increase the half-life of biochar in soil. This dissertation addresses the evaluation of biochars made from pinewood, peanut, and bamboo biomass by pyrolysis over different temperatures (300, 400, and 500 °C), and by hydrothermal conversion (HTC) at 300 °C. Furthermore, this dissertation investigates different methods of partial oxygenation procedures to re-incorporate oxygen functional groups during post-production treatment of biochar samples through the use of either H₂O₂ or O₃ treatments.

Biochars produced from pinewood, peanut and bamboo via pyrolysis were found to have lower CEC, higher pH, and lower O:C ratios when compared to biochars produced by HTC. Upon analysis it was found that a very strong correlation between O:C ratio and CEC exists, as illustrated by both elemental analysis and FTIR-ATR spectra. It was concluded, however, that while HTC produces a very high quality biochar in terms of CEC, there are predominant problems in using large scale HTC for producing biochars due to high cost of equipment and high pressures involved.

Biochar produced from pinewood biomass at 400 °C via pyrolysis was subjected to varying concentrations of H₂O₂ (1, 3, 10, 20, 30% w/w) or varying durations of O₃ gas flow (30, 60, 90 mins). In both partial oxygenation treatments, the treated biochar exhibited a lowering of pH and increase in CEC, with slight changes in both FTIR-ATR spectra as well as elemental analysis. These results reveal that the aforementioned partial oxygenation procedures were effective in increasing CEC while keeping the inherent stability of the biochar stable by leaving the bulk of the biochar composition unchanged in terms of O:C ratio.

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This dissertation is dedicated to a lifelong preservation of curiosity.

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CHAPTER I

INTRODUCTION

Biochar is the carbon rich solid by-product of biomass pyrolysis. While very similar to charcoal in both structure and physiochemical properties, biochar differs in that it is produced primarily for the application of improving soil quality as well as the long term sequestration of carbon in a stable form (Lehmann and Joseph, 2015). In recent years, research into biochar and its potential uses has been greatly expanded. Primarily, much interest in biochar can be broken down to several main categories: use as a carbon sequestration agent, use as a medium for the removal of unwanted materials (both organic and inorganic) in wastewater, and as a soil amendment for the increase of cation exchange capacity (CEC), soil fertility, and water retention (Smith, 2016; Mohan et al., 2014; Huff et al., 2014; Abel et al., 2013).

The production of biochar can be carried out in a wide variety of methods, but as a general rule biochar is produced by introducing organic waste into a system which is then heated to at least 300 °C with limited exposure to oxygen. The importance of establishing a lower threshold temperature for the production of biochar is that it separates what can truly be defined as biochar as opposed to material which has been simply torrefied (Kambo and Dutta, 2015). Some of the more popular methods to industrially produced biochar include the use of continuous reactors such as a rotating augur reactor, or non-continuous (batch type reactors) such as fluidized bed or rotating kiln reactors (Lehmann and Joseph, 2015). For laboratory production of biochar on a small scale, oftentimes batch reactors or tube furnaces are used. It should also be mentioned here that certain types of reactors can be modified to withstand high pressures, and have been used to create what is known as hydrochar- a material very similar to biochar, but made through the use of sub-critical to supercritical water as the reaction medium, instead of a

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simple inert atmosphere. The decision of what type of reactor to use is determined mainly based on the properties of the biochar, amount of biochar desired, and the energy consumption inherent to using the reactor in terms of heat production. In the special case of hydrochar production, the initial biomass introduced into the reactor does not have to be dried before use, and therefore plays a large role in the choice of reactor.

Generally, biomass pyrolysis results in three main products, consisting of biochar (solid residue), bio-oil (liquid residue), and syngas. Depending on the desired product, different types of pyrolysis can be utilized (Kan et al., 2016). The various types of pyrolysis are broken down into slow pyrolysis, fast pyrolysis, and gasification. Slow pyrolysis involves long residence times (hours to days long) and relatively low temperatures (300-700 °C). Fast pyrolysis is performed using very high rates of heating and very short residence times (~2s). Finally, gasification is performed at very high temperatures (~1100 °C). Each of these methods is used to generate a larger percentage by mass of the desired pyrolysis product: slow pyrolysis generates a higher amount of biochar, fast pyrolysis generates a higher amount of bio-oil, and gasification generates a higher amount of syngas, by percentage (Kan et al., 2016). As previously discussed, biochar is used primarily as a soil amendment. Interest has been placed in the production of bio-oil and syngas for energy production. Additionally, when choosing a method of pyrolysis and desired pyrolysis products, it is important to consider the biomass feedstock which will be utilized. Conventionally, biomass feedstocks such as solid waste, animal litter, crop residues, and woody biomass are used for pyrolysis (Ahmad et al., 2014). Various research has been performed concerning materials as ranging from pinewood, apricot stones, chicken litter, and solid waste and the conversion of said materials to biochar, further establishing the concept that biochar can be generated from wide-ranging types of materials (Li et al., 2015; Demiral and Kul,

2014; Lima et al., 2015; Huff et al., 2014). It has been noted that materials that are higher in lignin tend to produce higher amounts of biochar, resulting from the inherent chemical stability of lignin (Sohi et al., 2010). Such considerations are important in the optimization of desired pyrolysis by-products.

When considering the production of biochar, it is also valuable to understand the mechanisms by which biomass is converted into pyrolysis products. Since biomass is composed of cellulose, lignin, and hemicellulose, different reactions will take place dependent on the ratio of the three constituents (Caballero et al., 1997). Put simply, biomass with a greater percentage of lignin will behave differently than biomass predominately comprised of cellulose, and so forth (Smith et al., 2016). While various biomasses yield different compositions of by-products, the general mechanism is as follows: evaporation of free water content, primary decomposition, such as depolymerization, decarboxylation, charring, and aromatization, followed by secondary cracking (Kan et al., 2016). The primary decomposition and secondary cracking steps can occur at the same time which results in a complicated, interdependent process, which makes it difficult to predict the resultant species produced by pyrolysis. As mentioned above, the three main materials which make up biomass react differently, for instance: hemicellulose decomposes first, beginning around 250 °C, followed by cellulose, at around 325 °C, followed by the decomposition of lignin at around 350 °C (Morgan and Kandiyoti, 2013). Not surprisingly, other variables also effect the reaction pathways that biomass undergoes during pyrolysis. Heating rate, highest treatment temperature (HTT), retention time, gas flow rates, head space volume, and reactor type are all factors that may change the final product percentages and composition of biochar, bio-oil, and syngas. Much interest has been placed into controlling these variables in order to better control the final products, and has yielded a wide array of research projects. As is

apparent, though, the processes are very complicated and interdependent, so that there is no one single defining mechanism available over a broad set of experiments.

As a carbon sequestration agent, biochar is particularly attractive due to its inherent long-lived nature in soils. With growing concern over anthropogenic CO₂ emissions, biochar has garnered much interest as a material that can be made out of waste biomass which would otherwise decompose and return to the atmosphere as CO₂. Currently, naturally produced CO₂ is in a yearly dynamic equilibrium of roughly 5.5×10^{16} g, with an additional emission of carbon due to the burning of fossil fuels of 5×10^{15} g (Novotny et al., 2009). Essentially, the production of biochar intercepts the carbon cycle in such a way that it is truly “carbon negative” (Lee, 2012). Other such carbon capture methods, such as pumping CO₂ underground, may approach being carbon neutral, but could never actually be carbon negative. One of the main drawbacks in other forms of carbon sequestration is the fact that capture, transport, and storage are all processes which require energy to perform- energy provided primarily in the form of burning even greater amounts of fossil fuels, further exacerbating the very issue the process is trying to solve. Conversely, the production of biochar can be said to be exergonic- in that it is both spontaneous and exothermic. This means that the production of biochar can be driven by the heat released during biomass conversion, and in a continuous fashion. This conversion process is therefore highly efficient in terms of CO₂ capture in that no other sources of CO₂ are being utilized in the formation of the biochar. It must be said though, that this presupposes an already efficient reactor wherein the heat lost to the surroundings is relatively low. Biochar has been generated for millennia, as seen by the discovery of “Terra Preta” in the Amazonian basin- wherein biochar has been used to increase soil fertility by preventing weathering and increasing nutrient retention. While “Terra Preta” does increase soil fertility it must be understood that in

terms of efficiency as a carbon sequestration agent the method by which the pyrolytic carbon is made plays a large role. In the generation of “Terra Preta,” primarily what is known as the “slash and burn” technique was utilized. Slash and burn is a method by which biomass is simply cut down and burned where it lies, and little to no attempt is made to limit the exposure to oxygen. This, of course, leads to very low general yields of biochar, and releases much of the biomass as CO₂, making it extremely inefficient in terms of carbon capture. Therefore, it is necessary to utilize more advanced biomass to biochar conversion processes on a large scale in order to offset anthropogenic contributions to the global atmospheric carbon pool. Another interesting aspect in the discovery of “Terra Preta” is that it establishes the longevity of biochar in soils as being extremely long. It has been reported that biochar has an expected half-life in soils is at least thousands of years (Spokas, 2010). The long half-life of biochar is due in no small part to the thermodynamically stable structure of biochar, which resembles graphite modified primarily with oxygen functionalities such as carboxylates, lactones, and quinones (Keiluweit et al., 2010; Li et al., 2013). This stability of biochar in soil is critical when considering it for long term carbon sequestration. Being comprised of mostly aromatic carbon, biochar is able to resist physiochemical changes brought on by many biological processes as well as chemical induced processes such as exposure to light, various chemical treatments, and weathering to some degree. In contrast, the half-life of most biomass sources is limited from months to years, depending on the circumstances. One of the primary functions to consider when trying to gauge the stability of biochar in soil is the O:C ratio (Spokas, 2010). It is clear with the addition of various oxygen containing functional groups such as ether/ester linkages, lactone groups, etc., the aromaticity of the biochar is lessened, which allows for various other reactions to occur later, further degrading the biochar. To further elucidate; it is expected that biochars with and O:C ratio will have an

expected half-life of over 1000 years, biochars within an O:C range of 0.3-0.5 have an expected half-life of 100-1000 years, and any biochars with an O:C ratio greater than 0.6 only have an expected half-life of less than 100 years (Spokas, 2010). However, it is also important to understand the trade-offs when incorporating oxygen groups. In order to produce biochar with little to no oxygen groups, higher heating temperatures must be achieved, which is of course, a further energy cost which lessens the efficiency of the biochars ability to offset carbon emissions. Furthermore, biochar with little no oxygen groups, while having a very long half-life, is not as chemically reactive in terms of beneficial soil interactions such as increased CEC, water retention, and contaminant remediation (Huff and Lee, 2016).

As mentioned above, a second main use of biochar is that of a filtration medium. Due to the low-cost of production of biochar, especially when compared to use as an alternative to activated carbon, biochar is a very attractive material when it comes to filtration applications. The use of biochar in wastewater remediation can be broken down into two main categories based on the material which is to be removed; organic or inorganic materials. The organic component to be removed through biochar includes large aromatic materials, such as polycyclic aromatic hydrocarbons as well as organic dyes. The inorganic portion in wastewater often is comprised of deleterious metal species such as lead or cadmium, or less toxic species such as calcium and magnesium which are important considerations in water softening applications. The primary mechanism by which unwanted materials are removed from wastewater by biochar is through adsorption or precipitation, which are surface mediated functions. Therefore, much interest has been paid in the modification or activation of the surface of biochar in order to make the materials more suited to the aforementioned applications.

Currently, due to the expanding need to mitigate wastewater discharge containing

deleterious materials from various industries, much interest has been placed in the development of inexpensive and effective materials in order to do so. As contaminants can be either inorganic or organic, as well as have various charge states, levels of aromaticity, polarity, etc., it is therefore necessary to have a wide array of materials that can remove said contaminants, or ideally, have a method by which a common material can be modified to remove different contaminants. Currently, several methods are employed for contaminant removal, including flocculation, coagulation, adsorption via activated carbon, UV radiation, as well as the use of ozone (Bolong et al., 2009). Obviously, each of these methods is going to have their advantages and drawbacks depending on the nature of the contaminant being removed. Specifically for the removal of contaminants by use of activated carbon, which biochar can be considered a close analogue, one must consider the mechanisms by which species are immobilized by the addition of activated carbon/biochar. A recent report postulates that biochar has 4 main mechanisms by which it interacts with organic materials: electrostatic interactions, non-polar attraction, polar attraction, and partitioning (Ahmad et al., 2014). As mentioned later in this dissertation, many studies have been performed using methylene blue as a model organic compound in monitoring the capacity for its removal from wastewater with biochar (Ding et al., 2016b; Güzel et al., 2017; Li et al., 2016). Methylene blue can be thought of as a model compound because it contains both aromatic groups as well as a net positive charge, meaning that it can be used to evaluate biochars ability to interact with certain contaminants through π - π stacking, as well through electrostatic interactions. Inorganic contaminants are also a widespread issue, especially in developing areas, and much attention has been paid in the development of biochars with the capacity to remove contaminants such as lead, arsenic, copper, cadmium, and even radioactive species such as uranium (Ding et al., 2016b; Komkiene and Baltreinaite, 2016; Kumar et al., 2011). As with the

removal of organic species, biochar interacts with inorganic species by four primary means: anionic attraction, cationic attraction, ion exchange, and precipitation (Ahmad et al., 2014). The first three of these interactions are electrostatic in nature, and are heavily influenced by the types and quantities of various functional groups on biochar's surface. It should be noted that many biochars contain high amounts of various species which make up what is known as the "ash content" of the biochar which is the inorganic portion remaining after pyrolysis from the initial biomass. The ash content is an important consideration, especially concerning the mechanisms of ion exchange and precipitation, as some of the more common components of the ash content are anions such as PO_4^{3-} , OH^- , SO_4^{2-} , and CO_3^{2-} -species which can cause insolubility after binding to various cationic species (Zhou et al., 2016). The pH of the environment being treated is also another important aspect when dealing with the immobilization of inorganic contaminants. Almost all pyrolytic biochars have a pH that is basic, and depending on the amount of biochar applied, it is possible in certain circumstances to raise the pH of a water body high enough in order to immobilize metal contaminants through simple precipitation.

One of the most crucial characteristics to consider for the removal of both inorganic and organic contaminants is that of the surface area of the biochar. The mechanisms listed above are mostly surface mediated, so it follows that having a much higher surface area would concurrently lead to greater effectiveness of contaminant removal. Surface area is one of the defining characteristics that separates activated carbon from biochar; activated carbon tends to have very high surface area ($700\text{-}1000\text{ m}^2\text{g}^{-1}$), while biochar tends to have moderate to low surface area ($10\text{-}300\text{ m}^2\text{g}^{-1}$) (Inyang and Dickenson, 2015; Mohan et al., 2014). Of course, while activated carbon may be more effective at removing contaminants from wastewater, the trade off to using activated carbon over biochar becomes evident when considering cost: \$1500/ton

compared to \$246/ton, respectively (Inyang and Dickenson, 2015).

The third primary use of biochar is that of a soil amendment in order to increase soil fertility, CEC, and water retention (Abel et al., 2013; Ding et al., 2016a). It has been shown that the application of biochar in field studies can greatly increase crop yields (Jeffery et al., 2015). One of the reasons that the application of biochar can increase soil fertility is the ash content; biochar contains some of the essential nutrients for plant growth. It is important to consider that the ash content is a relatively short lived benefit, as once the ash content is solubilized and utilized for crop growth; it is no longer available in the soil. Even if not utilized for plant growth it is also possible for the ash content to become solubilized and therefore simply leach out of the soil. Longer term benefits from biochar application result from an increase in the overall CEC, as well as an increase in the water retention in soils. Water retention is a growing concern in agriculture, as with rising populations requiring more and more farmland, more water will then be used for crop growth. It is then essential to use water resources carefully, and if possible to use less water altogether. Biochar allows for less water to be used in great part due to its porous structure; water can be trapped in the pore volume of biochar and therefore not be as easily lost. Additionally, there could be attractive forces between the water and the exterior surfaces of biochar, leading to even greater water retention. A recent study has shown that biochar can increase the water holding capacity of soils by 18.4% overall, which is a substantial improvement over the untreated soil's water holding capacity (Abel et al., 2013). CEC is also an important factor when dealing with soils for agricultural use because it determines how effective a soil is at holding onto valuable nutrients. Simply put, it is essential to try to retain important cations critical to plant growth in a field setting, and this can be effectively done by increasing the CEC of the field as a whole, thereby mitigating leaching of nutrients that would otherwise

naturally occur. Biochar is an attractive substrate for use in increasing CEC due to its inherent overall negative charge in solution, due primarily to oxygen-functional group moieties found at the surface of the biochar. Much effort has been made in quantifying the various parameters throughout the production of biochar that yield biochars with high CEC. One of the most helpful, yet simple, indicators of high CEC is a high O:C ratio within a biochar sample (Lee et al., 2010).

In order to further enhance important characteristics of biochars such as surface area and CEC, post-production techniques have also been used. Such techniques include chemical activation of the biochar through the harsh treatment with KOH or H₂SO₄, or physical activation through the use of steam (Kambo and Dutta, 2015). Many of these post-production techniques are unfavorable on a large scale due to the generation of unwanted by-products and the high cost of the treatment chemicals (Zhang et al., 2004). Usually, activation techniques seek to change the structure of the biochar by greatly increasing surface area, while the overall chemical composition is left relatively the same. Other techniques can be used to alter not just the structure of the biochar, but also the functionality of the biochar itself. Such techniques include the use of ozone and hydrogen peroxide in order to add oxygen functionality, or the use of HNO₃ and NH₃ at high temperatures to add nitrogen functionality (Nguyen and Lee, 2016; Smith et al., 2015). Adding functional groups selectively to the surface of biochar can allow for the “tuning” of biochar properties. By controlling the functionality, it is possible to increase or decrease biochar’s ability to interact with various chemical species such as cations or anions, vary hydrophobicity, as well as changing the pH of the biochar.

The focus of this dissertation is to further evaluate the importance of O:C ratio of biochar samples in terms of stability, CEC, and water retention. In order to do so, a direct comparison of

biochars made from various feedstocks, temperatures, and production methods (both pyrolysis and hydrothermal conversion). Furthermore, this dissertation investigates the use of both ozone and H_2O_2 in an effort to produce greater amounts of oxygen containing functional groups primarily on the surface of the biochar in order to increase CEC, while maintaining the bulk stability of the biochar. Additionally, through the use of ozone and H_2O_2 , and the inherent short half-lives of said species, oxygen functionality will be introduced without producing any long-term harmful by-products. The use of advanced analytical techniques such as elemental analysis, FTIR-ATR, and Raman provide a detailed analysis as to the functional groups present in biochar samples, as well as the overall chemical composition of the samples. Throughout this dissertation I will demonstrate the viability of the usefulness of partial oxygenation of biochar with both H_2O_2 and ozone, as well as characterizing both treated and untreated biochars and providing a direct comparison of their physiochemical properties.

CHAPTER II

COMPARATIVE ANALYSIS OF PINEWOOD, PEANUT SHELL, AND BAMBOO BIOMASS DERIVED BIOCHARS PRODUCED VIA HYDROTHERMAL CONVERSION AND PYROLYSIS

Preface

The content of this chapter was published in the Journal of Environmental Management in 2014. The full citation can be found below. The publication has been modified in order to integrate the supporting information relevant to the publication into chapter.

Huff, M.D., Kumar, S., Lee, J.W., 2014. Comparative analysis of pinewood, peanut shell, and bamboo biomass derived biochars produced via hydrothermal conversion and pyrolysis. Journal of environmental management 146, 303-308.

1. Introduction

The conversion of biomass into biochar by either pyrolysis or hydrothermal conversion has been illustrated to be an important potential tool for both carbon sequestration and soil amendment (Day et al., 2005). Pyrolysis of biomass is usually divided into three main categories: slow pyrolysis, fast pyrolysis, and gasification. Slow pyrolysis is a more traditional means for the production of biochar, and involves the heating of biomass in the absence of oxygen over relatively long periods (≥ 30 minutes) of time at atmospheric pressure. Fast pyrolysis usually occurs on the order of a few seconds or minutes. Slow and fast pyrolysis can be implemented in many different types of reactors, some of the most used of these reactors

being batch or auger type. Gasification of biomass is carried out at much higher temperatures ($>700\text{ }^{\circ}\text{C}$) and is used to primarily to produce syngas and bio-oil. Hydrothermal conversion (HTC) is the practice of placing suitable biomass into a sealed vessel with water as a reaction medium, and then heating the vessel at low to moderate ($200\text{--}300\text{ }^{\circ}\text{C}$) temperatures (Sevilla et al., 2011; Titirici et al., 2012). Although the process has been known for close to a century, much interest has recently been paid to HTC as an efficient method for biomass conversion (Funke and Ziegler, 2010). Further research in HTC has been driven by the usefulness of the converted products, namely the use of biochar as a sorbent for toxic materials such as heavy metals (Hue et al., 2010; Kumar et al., 2011). Additionally, HTC as well as pyrolysis of biomass materials produce a bio-oil byproduct which can potentially be utilized as fuel (Mohan et al., 2006; Akhtar and Amin, 2011). The biomass is converted, under autogenic pressures, into biochar, a solid carbon-rich product. Both methods of synthesis take biomass which has a naturally relatively short lifetime and convert it to a carbon rich solid which has been shown to be stable over hundreds of years (Lehmann et al., 2006; Cheng et al., 2008; Nguyen et al., 2009). In choosing a biochar for soil amendment properties, and/or as a carbon sequestration agent, it is important to look at the characteristics pertinent to the desired application. One of the most important features when considering the use of biochar as soil amendment is its cation exchange capacity (CEC). Biochar with high CEC values are much more desirable in soils, as the biochar will allow for greater retention and availability of cations such as NH_4^+ and K^+ (Laird et al., 2010). As far as carbon sequestration is concerned, long term stability in soil is of major consideration. Attributes of biochar such as its fixed carbon content (percentage) and O:C ratio can serve as important factors in assessing the stability of these products on a long term basis (Keiluweit et al., 2010; Knicker, 2007; Elmquist et al., 2006).

The biomasses utilized in this study were pinewood, peanut shell, and bamboo. Pinewood and bamboo biomasses were chosen for reasons similar to those previously reported, in that wood residues make up for 39% of the total biomass available in the United States (Thangalazhy-Gopakumar et al., 2010). Additionally, the U. S. produces a large amount of peanuts annually, and given that peanut shells are a natural by-product of this process, it is important to look for ways to use this biomass beneficially.

Although biochar production by biomass pyrolysis has been quite well studied, reports on biochar production through HTC are relatively fewer (Funke and Ziegler, 2010; Hu et al., 2010; Akhtar and Amin, 2011). HTC of biomass into biochar could potentially be one of the potential technology options to achieve a “smokeless” biochar and biofuel production process, which would be desirable to minimize the potential impact on environmental air quality, especially in considering the envisioned biochar carbon sequestration at giga-tons-carbon (GtC) scales to control global climate change. It is essential to further understand the characteristics of biochars produced by HTC and pyrolysis from various feedstocks of biomass materials. In this paper, we report a comparative HTC vs. pyrolysis biochar production study in relation to the potential use of biochars as a beneficial soil amendment and potential carbon sequestration agent.

2. Materials and Methods

The types of biomass used in this study included pinewood, peanut shell, and bamboo, all of them were provided by Danny Day of Eprida Inc. The pinewood and peanut shell biomasses were in a pelletized form, while the bamboo biomass consisted of 1-2 cm long slivers. After receiving these biomass samples, all of them were dried at 70 °C in an electric oven for 48 hours before use for biochar production study.

Biomass was converted into biochar by pyrolysis or HTC using the same 500-mL hastelloy autoclave high-pressure batch reactor (Parr reactor) system equipped with proportional-integral-differential controllers (Regmi et al., 2012). Pyrolysis was carried out on each type of biomass at 300, 400, and 500 °C, respectively, using N₂ as a sweep gas. Heating of the reactor was carried out at a rate of 12 °C per min, and the highest treatment temperature (HTT) was held for 30 minutes during each trial. Biochars produced via pyrolysis were then collected after cooling the reactor to the room temperature and weighed directly to determine yield.

HTC was performed by placing biomass and water with a 1:3 mass ratio into the reactor. The reactor was then sealed and heated to 300 °C at a rate of 8 °C min⁻¹ and held at autogenic pressure conditions for 30 minutes. Once the reaction time was completed, the reactor was rapidly cooled utilizing an internal water coil. The biochars made via HTC were then removed from the reactor, filtered, and then dried overnight at 105 °C. The dried samples were then weighed to determine yield.

3. Products Analyses

3.1. pH determination

The pH of each type of biochar was measured by first taking a 20 g aliquot of biochar and suspending it in 80 mL of millipore water in 125mL Erlenmeyer flasks. The samples were then shaken at 100 rpm for 48 h. The pH of the resulting biochar/water slurry was then recorded.

3.2. Elemental Analysis

Representative samples of biochars produced from pinewood via pyrolysis at 300, 400, and 500 °C and via HTC were sent to the Galbraith Laboratories in Knoxville, TN, for proximate and elemental (C, H, and N) analysis.

3.3. Reference Soil Sample

The reference soil sample was provided by Dr. Charles Garten of Oak Ridge National Laboratory. This soil sample was collected from a surface soil of 0-15 cm deep at the University of Tennessee's Research and Education Center, Milan, TN (35°56'N latitude, 88°43'W longitude), which is also known as the Carbon Sequestration in Terrestrial Ecosystems site (CSiTE) supported by the US Department of Energy. The soil sample was autoclaved at 120 °C for 30 min prior to shipping and use in this study. Additional information pertaining to the soil sample is reported in reference (Lee et al., 2010).

3.4. Cation exchange capacity measurement

CEC refers to the number of exchangeable cations located on the surface of a given sample. The method of measurement utilized herein was that of compulsive barium loading, wherein barium is used in high concentration to essentially displace all other cation species on the surface of the biochar. The barium itself is then displaced via magnesium ions as well as competing protons during the assay, and the resultant CEC is measured by the change in the conductivity of the CEC assay medium. CEC measurement was carried out using a procedure modified from the method reported in Ref. (Lee et al., 2010) and (Skjemstad et al., 2008). Initially, all CEC measurements were carried out at a pH 8.5 and subsequently the pH was adjusted using 0.010M H₂SO₄ by half units until a final pH of 5.0 was reached. At each half point pH unit, successive CEC measurements were taken. A detailed procedure for CEC measurement is as follows: CEC measurements were carried out following protocols found in Ref (Lee et al., 2010 and Skjemstad et al., 2008). Accordingly, biochar samples were placed into 125 mL Erlenmeyer flasks with Millipore water initially at a weight/weight biochar-to-water

ratio of 1:4. These Erlenmeyer flasks containing the samples were placed on a shaker platform and shaken at 100 rpm for 48 hours, which was then followed by filtering the samples and drying the biochar materials overnight in an electric oven. The samples were then finely ground utilizing a household coffee grinder until a visibly uniform consistency was obtained. Aliquots of 0.5 g samples of each of these biochars were then placed into previously weighed 50 mL centrifuge tubes. To each of these centrifuge tubes was added 30 mL of 0.5M BaCl₂. The samples were then allowed to incubate in the centrifuge tubes on a shaker table at 100 rpm overnight. The samples were then pelleted at 20,000 rpm (48,384 x G) in a Beckman Coulter Avanti® J-26 XP centrifuge, using a JA 25.50 rotor for 15 min at 4° C. The samples were decanted (to retain the biochar materials) and then treated with an additional 30 mL of 0.5 M BaCl₂. This process was repeated 3 additional times. During the last 2 washes, each sample had the pH adjusted to 8.5 with the addition of 0.1M Ba(OH)₂ solution. After the fourth 0.5 M BaCl₂ loading, the samples were pelleted with centrifugation and the supernatant liquid was decanted carefully, retaining the biochar sample. The samples were then washed twice with 30 mL of 0.05 M BaCl₂, and 4 times with 30 mL of 0.002M BaCl₂ solution by suspension and pelleting of the biochar materials with centrifugation. After the last wash, the centrifuge tubes containing the biochar samples were placed upon a shaker platform at 100 rpm for 60 min. The samples were then centrifuged at 20,000 rpm (48,384 x G) and decanted, then dried in an oven for 48 h at 70°C.

After drying, each biochar sample was carefully reweighed. Each sample was then treated with 20 mL of 0.01 M MgSO₄ solution which has been pH adjusted to 8.5 using a solution of Ba(OH)₂ and reweighed to determine the exact amount of solution added. The samples were then returned to the shaker platform for another 20 h. At the end of shaking,

conductivity of each sample at pH 8.5 was measured using a conductivity meter. These measurements were compared to that of a standard 0.0015M MgSO_4 . If it was found that the value was lower than the standard, more 0.01M MgSO_4 solution would be added until the conductivity of the standard was matched. If the value were found to be higher, deionized water was added until the conductivity of the standard was matched. Once the conductivity was matched, samples (including the associated liquid medium) were then weighed for analysis. Samples were then treated with small amounts of 0.01M H_2SO_4 until the pH was reduced by a half unit. The conductivity was then measured again and made to match the standard. The samples were then reweighed, and this process was repeated over a pH range of 8.5 to 5. All samples were assayed six times ($n=6$) at room temperature. In order to calculate CEC, the following equation was used:

$$A = (\text{weight of } \text{MgSO}_4 \text{ solution in g}) * (1 \text{ g/mL solution}) * (0.02 \text{ M } \frac{1}{2} \text{ MgSO}_4)$$

$$B = (W_2 - W_1)(0.003)$$

$$\text{CEC} = (A - B) * (100) / (\text{sample weight in g})$$

Wherein, A is equal to the mmol of MgSO_4 added to each sample after barium loading. B is equal to the amount of equivalent monovalent cations of the remaining concentration of MgSO_4 , as calculated when W_2 is the weight of the sample container at the end of the titration and W_1 is the weight of the sample container and sample weight combined.

3.5. Methylene Blue Adsorption Assay

Methylene blue adsorption assays were performed in order to measure the interaction of biochar with a charged organic compound. These assays were performed using a modified procedure based on protocols published (Arami-Niya et al., 2011). Standard amounts (50 mg) of

previously ground biochar were placed into 50mL centrifuge tubes. To each biochar sample, aliquots of 30 mL 20mg/L methylene blue solutions were added. These samples (in 50mL centrifuge tubes) were then placed onto an *Innova 2300* platform shaker, and shaken at 100 rpm at room temperature for 48 h. After the allotted time, the samples were then centrifuged at 20,000 (48,384 x G) rpm for 10 min in order to pelletize any particulate. Aqueous portions of the samples were then placed into quartz cuvettes and UV-Visible measurements were taken with a Cary 5000 spectrophotometer at 665 nm. Each sample was taken in duplicate in order to reduce error in measurement. The concentration of remaining methylene blue in solution was measured by process outlined in reference (Arami-Niya et al., 2011). Average results (n=2) are reported.

$$Q_e = \frac{(C_o - C_e)V}{W}$$

Wherein, Q_e is the amount of methylene blue removed from solution as reported in mg/g biochar added, C_o and C_e are the initial and equilibrium concentrations (g/L), respectively, V is the volume of solution used, and W is the grams of biochar used.

3.6. IR-Spectroscopy

Infrared spectra were obtained with a Shimadzu IRPrestige-21 FT-IR spectrophotometer. Samples were placed into an ATR attachment utilizing a ZnSe trough. Spectra were collected over 256 scans, at a resolution of 4 cm^{-1} , and over a range of 750-4000 cm^{-1} .

4. Results and Discussion

4.1. Biomass Conversion Efficiencies

Table 1 reports the yield of each type of biochar either via pyrolysis or HTC calculated from the input dry weight of the biomass. As expected, biochar yield decreased with higher treatment temperatures. This is due to greater volatilization which converts a greater amount of biomass to bio-oil and gaseous products (Demirbas, 2004). The hydrothermally converted biomass shows the greatest percentage of biochar synthesized, which is also expected due to the higher pressures involved, which naturally favor the formation and retention of solid products (Berge et al., 2011).

Table 1. Percentage yield of biochar as a function of temperature, biomass, and process method.

Temperature °C	300	400	500	300
Process method	Pyrolysis	Pyrolysis	Pyrolysis	HTC
Pine	32.89 ± 0.22	27.26 ± 0	26.47 ± 0.08	49.51
Peanut	38.64 ± 1.12	33.64 ± 0.29	32.01 ± 0.13	50.07
Bamboo	33.25 ± 0.84	29.93 ± 0.21	28.75 ± 0.24	32.73

The pH of each type of biochar differed mainly on the basis on the type of synthesis, as shown in Figure 1. It is well known that the reaction pathway via pyrolysis yields alkaline biochar (Shafizadeh, 1982), while the reaction pathway of HTC yields an acidic biochar (Toor et al., 2011). Higher treatment temperatures yielded higher pH values when concerning biochars produced via pyrolysis.

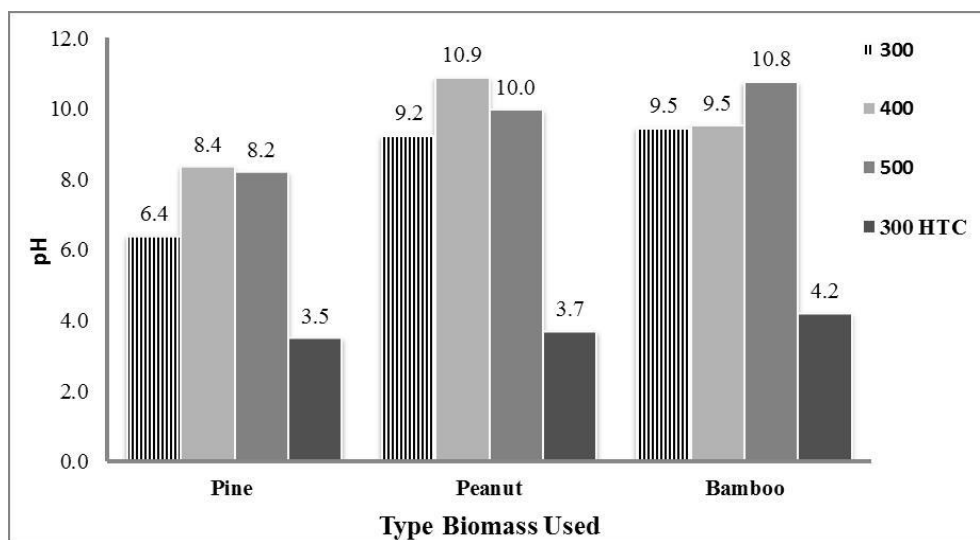


Fig. 1. pH of biochars as a function of temperature, and types of biomass.

4.2. Biochar FT-IR Analyses

FT-IR measurements revealed the biochar functional group differences in relation to the biomass thermal conversion processes. As shown in Figure 2, peaks about 1100, 1200, and 1670 cm^{-1} appear in the HTC biochars, but not in biochars produced via pyrolysis. The peaks at ~ 1100 and 1200 cm^{-1} correspond to C-O stretching and O-H bending modes of alcoholic, phenolic, and carboxylic groups (Pradham and Sandle, 1999). The peak at 1670 cm^{-1} is indicative of C=O stretching. All samples exhibit a peak at 1570 cm^{-1} , corresponding to C=C stretching, which is representative of the aromatic nature of the samples. Additionally, concerning the biochar samples produced via pyrolysis, there is a temperature dependence on the relative intensity of the peak at 1570 cm^{-1} , which indicates a greater amount of C=C bonds being formed as the HTT is increased. Also, an intense peak at 870 cm^{-1} found samples produced via pyrolysis can be attributed to aromatic C-H bending (Wag and Griffiths, 1985). Overall, the FT-IR spectra exhibit a higher retained amount of oxygen functional groups for HTC biochars, as well as a higher degree of aromatic functionality for biochars produced via pyrolysis.

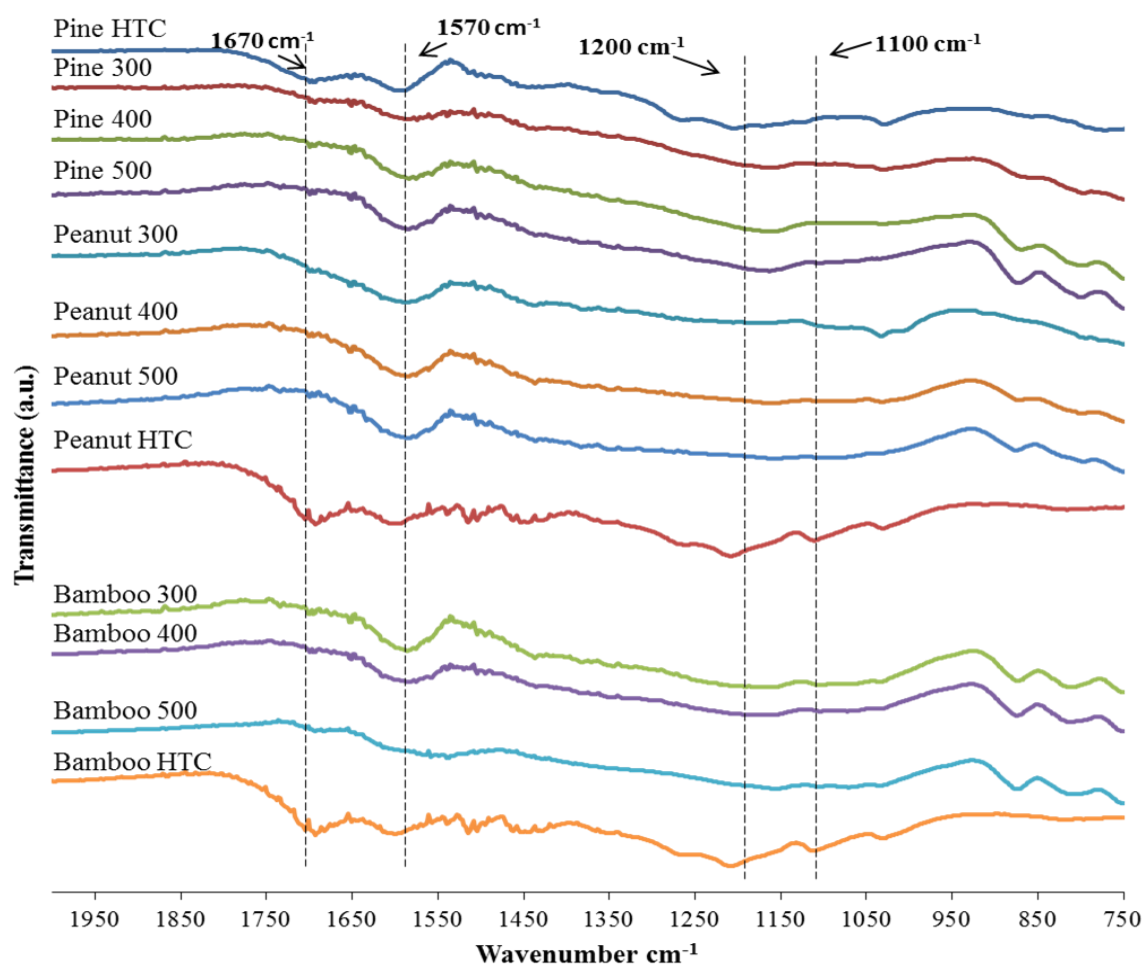


Fig. 2. FT-IR spectra of biochar samples.

4.3. Proximate and Elemental Analysis

Proximate analysis revealed a temperature dependence of volatile matter content for pine biochars produced via pyrolysis. Pine biochars were chosen as representative samples for proximate/elemental analysis. As Table 2 shows, as temperature was increased, volatile matter

content decreased substantially (27.89 %, 19.57%, and 11.67% for the biochars produced via pyrolysis at 300, 400, and 500 °C, respectively). By comparison, the biochar produced from pinewood via HTC retains a relatively high amount of volatile matter (46.72%). Furthermore, a similar pattern is seen in fixed carbon content, for biochars produced via pyrolysis in that increased temperatures yielded a biochar with higher fixed carbon percentages especially when comparing that of biochar produced at 300 °C (67.18%), to those produced at 400 and 500 °C (76.44% and 82.11% fixed carbon, respectively). The HTC biochar shows a much lower fixed carbon (50.8%), which is consistent with its relatively high amount of volatile matter (46.72%). Ash content percentages show a dependence on temperature for pine biochars produced via pyrolysis, 4.93%, 3.99%, and 2.37% for samples produced at 300, 400 and 500 °C, respectively. Pine HTC biochar has nearly the same value (2.39%) for ash content as the biochar produced by pyrolysis at 500 °C. The elemental analysis shows that a loss of oxygen atoms at higher temperatures, as well as a higher amount of oxygen retained for the biochar produced via HTC. This is correlated by the FT-IR spectra in which the peak at 1640cm^{-1} appears more intense in the HTC biochar, and much weaker in the biochars produced by pyrolysis, especially at higher treatment temperatures. Oxygen content was calculated by analysis, rather than by difference. The O:C mol ratio gives some idea as to the long term stability of biochar in soil (Arami-Niya et al., 2011), wherein the higher the ratio, the less stable the biochar. Typically, biochars with an O:C 0.2 or greater have half lives in soil of 100-1000 years, while biochars with O:C lower than 0.2 have half lives in soil greater than 1000 years (Spokas, 2010). The results of this analysis show that all pine biochars produced via pyrolysis are placed into the latter category, while the pine biochar produced via HTC belongs in the former category.

Table 2. Biochar Elemental and Proximate Analysis.

Sample	% loss on drying	% volatile matter	% fixed carbon (by difference)	% Ash	C%	H%	N%	O%	O:C (mol ratio)
Pine 300	4.08	27.89	4.93	67.18	74.17	3.76	<0.5	14.54	0.15
Pine 400	4.88	19.57	3.99	76.44	81.64	2.69	<0.5	5.26	0.05
Pine 500	4.29	11.67	2.37	82.11	83.2	2.74	<0.5	4.05	0.036
Pine HTC	3.71	46.72	2.39	50.8	66.45	4.2	<0.5	22.84	0.26

4.4. CEC of Biochar Samples

CEC was shown to be dependent on production process, highest treatment temperature, and biomass precursor. This assay allows for the comparison of biochar samples over a range of pH values, which is important due to the varying native pH of the samples, especially when comparing pyrolysis biochar samples with HTC biochar samples. The greatest impact upon CEC is shown by the comparison of HTC biochar versus that of biochars produced via pyrolysis. At pH 8.5, pine biochars produced at 300, 400 and 500 °C show CEC values of 13.474 ± 1.385 cmol Kg⁻¹, 8.991 ± 1.457 cmol Kg⁻¹, and 5.786 ± 3.620 cmol Kg⁻¹, respectively. Comparatively, HTC biochar has a CEC of 63.465 ± 3.658 cmol Kg⁻¹ at pH 8.5. A similar trend was observed for peanut and bamboo biochars. By comparison, the CEC of the reference soil at pH 8.5 was 16.174 ± 1.215 cmol Kg⁻¹. As shown in Figure 3, the HTC biochars resulted in the greatest CEC value when compared to the biochars converted via pyrolysis. The complete set of CEC data values measured for all 12 biochar samples and the reference soil can be found in Table 3.

Table 3. Average Cation Exchange Capacity values of biochar samples. The biochar cation exchange capacity was assayed using a compulsive barium loading followed by a magnesium displacement for each sample. Each value was determined as an average of n=6 trials. CEC values are shown in cmol kg^{-1} .

Sample ID	pH 8.5	pH 8.0	pH 7.5	pH 7.0	pH 6.5	pH 6.0	pH 5.5
Pine Char 300	13.474 \pm 1.385	12.871 \pm 1.543	11.893 \pm 1.734	10.959 \pm 1.969	10.062 \pm 1.800	9.155 \pm 1.876	8.473 \pm 1.795
Pine Char 400	8.991 \pm 1.457	8.537 \pm 1.483	7.512 \pm 1.438	6.799 \pm 1.390	5.755 \pm 1.239	4.939 \pm 1.133	3.797 \pm 1.170
Pine Char 500	5.786 \pm 3.620	4.807 \pm 3.970	4.039 \pm 3.936	3.170 \pm 4.151	2.575 \pm 4.365	1.887 \pm 4.479	1.183 \pm 4.671
Pine Char HTC	63.465 \pm 3.658	62.592 \pm 3.457	60.878 \pm 3.587	58.519 \pm 3.366	56.096 \pm 3.408	53.844 \pm 4.533	46.054 \pm 6.527
Peanut Char 300	37.190 \pm 6.202	36.201 \pm 6.207	35.177 \pm 6.359	34.416 \pm 6.314	33.310 \pm 6.156	31.782 \pm 5.892	29.555 \pm 4.850
Peanut Char 400	13.014 \pm 0.496	11.966 \pm 0.829	11.417 \pm 0.721	10.471 \pm 0.570	9.539 \pm 0.632	8.704 \pm 0.810	7.739 \pm 1.207
Peanut Char 500	12.169 \pm 3.067	11.626 \pm 2.980	11.033 \pm 3.205	10.083 \pm 3.522	9.282 \pm 3.803	8.532 \pm 4.078	7.655 \pm 4.172
Peanut Char HTC	56.728 \pm 8.902	54.864 \pm 9.793	52.410 \pm 10.420	50.629 \pm 10.967	47.958 \pm 10.847	45.740 \pm 10.614	43.285 \pm 9.343
Bamboo Char 300	29.243 \pm 4.003	27.990 \pm 4.312	27.123 \pm 4.260	25.810 \pm 3.857	24.733 \pm 3.805	23.868 \pm 3.968	22.856 \pm 3.926
Bamboo Char 400	18.397 \pm 2.787	17.839 \pm 2.768	16.910 \pm 3.013	16.381 \pm 2.994	15.826 \pm 2.967	15.273 \pm 3.034	14.289 \pm 3.228

Table 3. Continued

Bamboo Char 500	12.199 ± 1.575	11.552 ± 1.512	10.643 ± 2.058	9.991 ± 2.434	9.318 ± 2.557	8.475 ± 2.691	7.753 ± 3.171
Bamboo Char HTC	41.597 ± 12.656	40.455 ± 13.008	38.903 ± 12.802	37.657 ± 12.340	36.284 ± 11.812	34.590 ± 10.904	31.383 ± 10.752
Soil Reference	16.174 ± 1.215	15.316 ± 1.198	13.944 ± 1.293	11.729 ± 1.680	9.382 ± 1.980	8.063 ± 1.902	6.625 ± 1.851

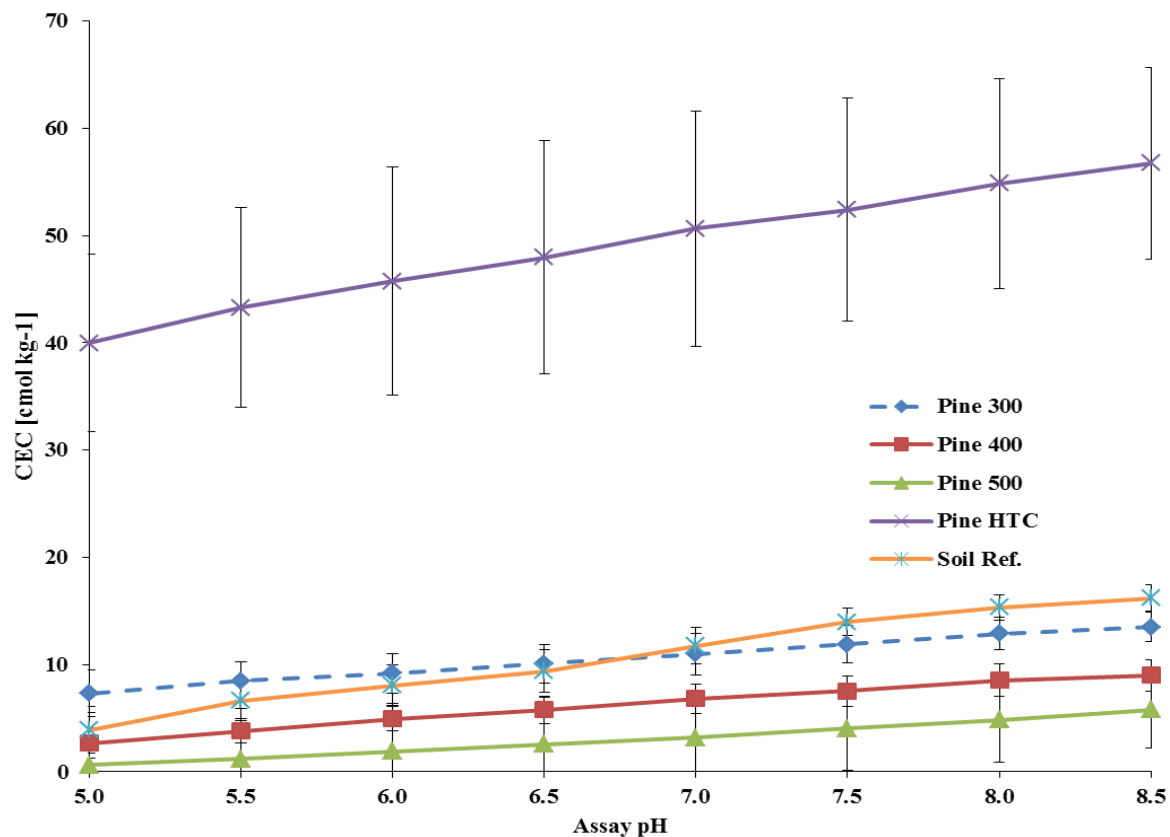


Fig. 3. CEC of biochars derived from pinewood biomass and soil reference sample.

In comparing biochars produced via pyrolysis at different pyrolysis temperatures, there is a clear relationship between HTT and CEC, that being the lower the temperature, the higher the CEC. This correlates with the loss of oxygen functional groups as measured by FT-IR over increasing HTT. This data also corresponds well with the O:C mol ratio as determined by elemental analysis. Retained oxygen content correlates with higher CEC values, as shown in Figure 4. All biochar CEC assays show a dependence on pH. At lower pH values, protons compete with bound cations on the biochar surface, thereby driving the cations off the sample surface and into solution.

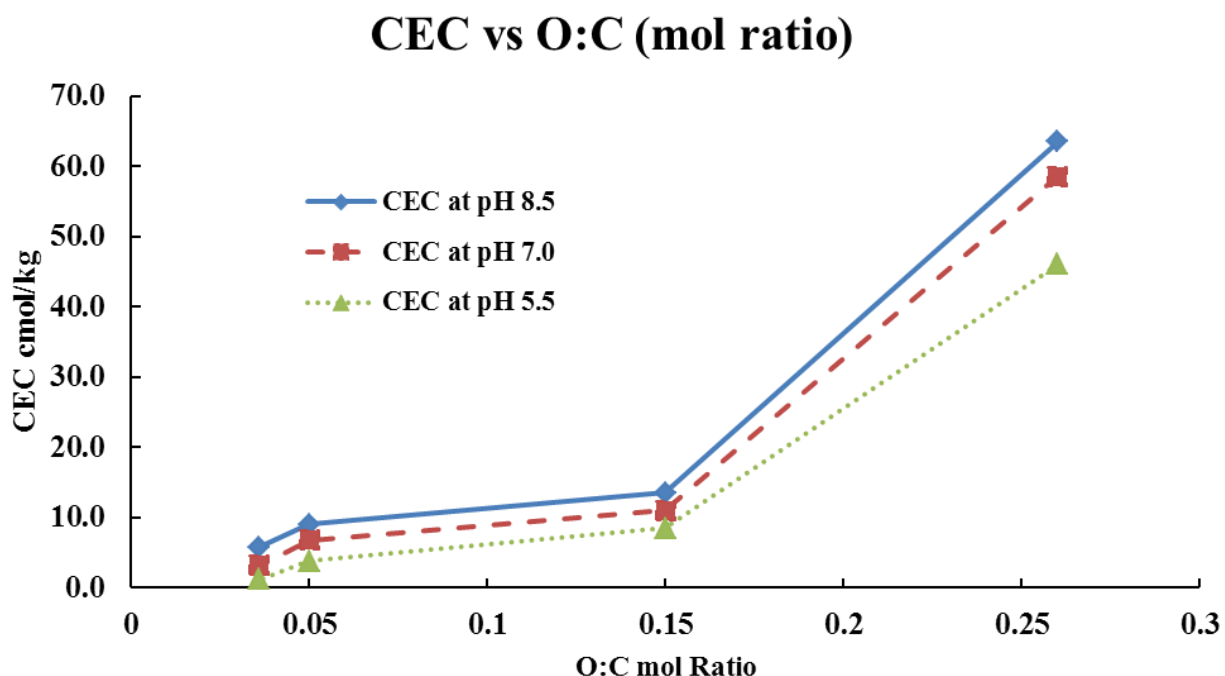


Fig. 4. CEC of pinewood-derived biochar samples as a function of O:C mol ratio for a range of pH values.

4.5. Methylene blue adsorption

The observed methylene blue adsorption results show that there is greater affinity for methylene blue onto biochars produced via pyrolysis at 300 °C as compared to biochars produced at 400 and 500 °C. Furthermore, the results indicate a greater correlation as to which biomass precursor was used over synthetic route used. There seems to be no clear correlation between biochar's CEC and methylene blue adsorption, as shown in Fig. 5. Previously published results suggest that the mechanism for dye adsorption onto biochar is dependent on dispersive π - π interactions between the graphene-like sheets of the biochar with the aromatic

ring structure of the dye (Qiu et al., 2009). The molecular structure of methylene blue contains a type of aromatic ring structure in addition to the positively charged amine group (cation). Pine biochars produced via pyrolysis showed the lowest methylene blue adsorption at an average range of 1.1 (300 °C)-2.5 (500 °C) mg/g of biochar, while peanut biochars produced by pyrolysis show the highest amount of adsorbed methylene blue, ranging on average from 3.7(300 °C)-6.7(500 °C) mg/g of biochar. The pine biochar produced by HTC shows the highest amount of adsorbed methylene blue (5.8 mg/g of biochar) when compared to the 3.5 mg/g and 4.6mg/g for the HTC peanut and bamboo biochars as shown in Table 4.

Table 4. Methylene blue adsorption onto biochar samples (units of mg of methylene blue removed/ g biochar, results in duplicate).

Temperature °C	300	400	500	300
Process method	Pyrolysis	Pyrolysis	Pyrolysis	HTC
Pine	2.54 ± 0.966	1.82 ± 0.214	1.16 ± 0.494	5.81 ± 0.092
Peanut	6.76 ± 0.006	5.22 ± 0.264	3.69 ± 0.408	3.51 ± 1.288
Bamboo	4.78 ± 0.148	3.58 ± 0.176	3.88 ± 0.138	4.67 ± 0.987

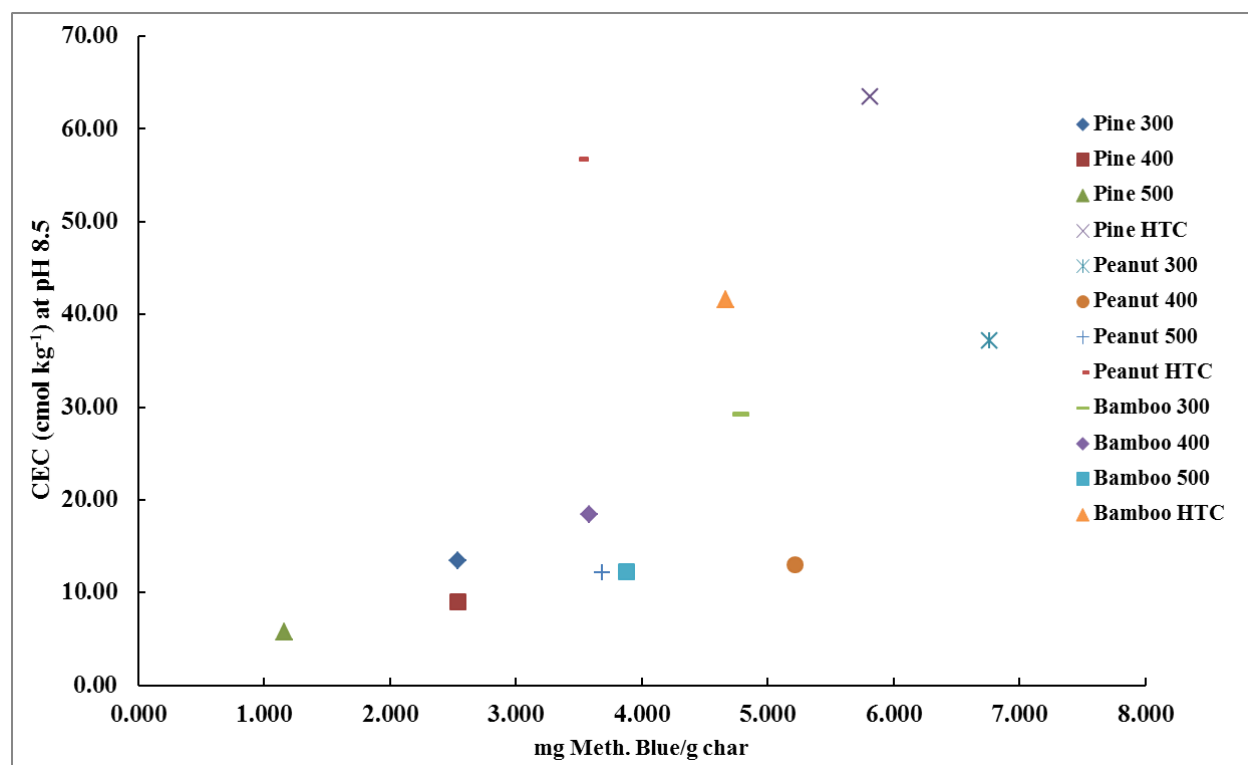


Fig. 5. Plot of CEC values at pH 8.5 versus methylene blue adsorption onto biochar samples.

5. Conclusions

All biochars produced by HTC had CEC values higher than that of the soil reference, as well as did peanut shell and bamboo biochars produced by pyrolysis at 300 °C and bamboo at 400 °C. The CEC value of the HTC biochar appears correlated with its oxygen functional group content as indicated by its O:C ratio and the FT-IR results. In addition, all biochars produced also show some affinity for the removal of methylene blue from solution, although it appears that the type of biomass used, rather than process treatment dictates the effectiveness of adsorption of methylene blue from solution. These results indicate the possibility of the use of these biochars for the potential removal of certain organic molecules such as dyes in water. As shown by proximate analysis, much higher fixed carbon content is created in biochars produced by pyrolysis, and is a function of highest treatment temperature as noted by previous reports (Demirbas, 2004; Hossain et al., 2011). Percent volatile matter follows the same trend as fixed carbon content as well. Quite interestingly, biochars produced by HTC tend to retain much higher oxygen content when compared with biochar produced from the same biomass via pyrolysis. CEC values for biochars produced by HTC were much higher when compared with biochars produced via pyrolysis, a trend that fits well with the O:C ratio. Future studies to comparatively analyze the potential biochar toxin content in these biochar materials will help to determine their viability for use as soil amendments.

CHAPTER III

BIOCHAR-SURFACE OXYGENATION WITH HYDROGEN PEROXIDE

Preface:

The content of this chapter was published in the Journal of Environmental Management in 2016. The full citation can be found below. The publication has been modified in order to integrate the supporting information relevant to the publication into chapter.

Huff, M.D., Lee, J.W., 2016. Biochar-surface oxygenation with hydrogen peroxide.
Journal of Environmental Management 165, 17-21.

1. Introduction

Biochar has recently been the focus of much research interest concerning its ability as a carbon sequestration agent as well as a soil amendment. Biochar is the solid product formed from the pyrolysis of biomass, along with bio-oil, and gaseous products. Much interest has been placed on biochar due to its capacity to act as an inexpensive analogue to activated carbon, and as such, been explored in its usage as a medium for the removal of heavy metals and dye molecules from wastewater systems (Mohan et al., 2014). Further interest in biochar is driven by its use as a soil amendment, by being able to increase the agronomic value of soils by increasing the cation exchange capacity (CEC) as well as the water retention properties of soil (Lehmann and Joseph, 2012). It has been shown that the CEC and lifetimes in soil of biochar is related to its retained oxygen content through pyrolysis (Spokas, 2010). Additionally, higher O:C ratio correlates with higher CEC (Lee et al., 2010).

Much like with activated carbons, many different attempts have been made in order to “activate” biochar to increase its heavy metal and dye adsorbing capacity (Beesley et al., 2011; Mohan et al., 2014). These methods include the use of harsh acids and bases such as phosphoric acid and potassium hydroxide for example (Azargohar and Dalai, 2008; Uchimiya et al., 2010). However, many of these processes are prohibitively expensive at a large scale, or produce deleterious byproducts. Recently, it has been shown that hydrochar (biomass converted to a solid carbon rich material through hydrothermal conversion) treated with H_2O_2 had an increased capacity adsorb metals from solution (Xue et al., 2012). H_2O_2 is a strong oxidant, which is relatively inexpensive and clean. It is attractive to use H_2O_2 as a method to modify the properties of biochar. After being employed, it would unlikely remain in the biochar materials as adverse residues since H_2O_2 can decompose to the clean products of H_2O and O_2 . Our previous work also suggested the use of peroxides including H_2O_2 for partial oxygenation of biochar to enhance its cation exchange capacity (Lee et al., 2013).

In this study, biochar derived from pinewood biomass was produced via pyrolysis at 400 °C and then treated with varied concentrations of H_2O_2 ranging from 1% to 30% (W/W). Pinewood biomass was used through pyrolysis to produce the biochar sample materials due to it being plentiful and locally available. The highest treatment temperature (HTT) of 400 °C was chosen for pyrolysis due to it being one of the most common HTTs used for slow pyrolysis, and is neither so low of a temperature that would result in incomplete conversion of the biomass (torrefaction), nor so high a temperature that there is little retained oxygen functionality through pyrolysis (Amutio et al., 2012; Ben and Ragauskas, 2012). The biochar samples were treated with H_2O_2 solution to test the effects of partial oxygenation on biochar with respect to CEC, field water-retention capacity, and dye adsorption. Since biochar is considered as a potential

replacement for activated carbons as dye absorbents due to its low comparative cost, methylene blue was tested as a model dye compound. Methylene blue has been widely used in adsorption studies on a wide range of substrates, such as biochars, activated carbon, and hydrochars (Mohan et al., 2014; Rafatullah et al., 2010). This research also investigates the elemental composition of the biochar samples both pre-and-post H₂O₂ treatments in order to evaluate the possible change in biochar through partial oxygenation processes.

2. Materials and methods

For this study, pinewood biomass was obtained locally on the Old Dominion University campus by sawing fresh limbs of an eastern shore pine tree. The limb was then segmented into a more usable size and then dried at 105 °C in an electric drying oven until any residual water had been removed. The wood was then broken into chips of various sizes of 3-5 cm long and roughly 1 cm in thickness prior to their use in pyrolysis for biochar production. Pyrolysis of pinewood biomass for biochar production was carried out in a 500 mL hastelloy autoclave high pressure Parr reactor, which was set up for use at atmospheric pressures. A flow of N₂ gas was used prior to heating the vessel in order to expel any other gasses from the reactor. The reactor was then heated until 400 °C was reached. Once the highest treatment temperature was reached, the temperature was held for 30 minutes. After 30 minutes had elapsed, the reactor was cooled using an internal water coil, while the biochar was kept under a flow of N₂ to prevent atmospheric gas backflow. Once cooled, the reactor was opened and the biochar was removed and weighed for biomass-to-biochar yield analysis. In total for this study, the biomass was converted to biochar over 5 syntheses (batches). After each synthesis, the biochar was removed from the batch reactor and weighed. Overall 36.646% \pm 0.633 of the biomass was converted into

biochar through pyrolysis by mass.

Before further use, 50 gram aliquots of biochar samples were rinsed and filtered with 3 portions of 200 mL of Millipore water and then dried at 105 °C overnight in an electric drying oven. This rinsing was performed to remove any water extractable substances that may interfere with later assays. After drying, the biochar was then physical grinded utilizing a simple household coffee grinder followed by use of a mortar and pestle until the biochar could be passed through a 106 μm sieve (U.S.A. Standard Testing Sieve NO. 140).

Treatment of biochar with H_2O_2 in water was carried out in a method similar to that reported by Xue, Yingwen, et al. Briefly, biochar samples were placed into 125 mL Erlenmeyer flasks and aliquots of H_2O_2 solutions were added to each sample with a 1g biochar/20 mL solution ratio. H_2O_2 solutions were varied by concentration. Overall 1, 3, 10, 20, and 30% w/w treatments of H_2O_2 were used, as well as an experimental blank consisting of just biochar and Millipore water in the same ratio as listed above. Each sample was transferred to in a 50-ml plastic centrifuge tube, capped, and placed on an *Innova 2300* platform shaker to shake for 2 hours at 110 rpm. After 2 hours of shaking had elapsed, each sample was then filtered through Fisherbrand® P8 filter paper and rinsed with 3x100 mL portions of Millipore water to remove any residual H_2O_2 . The samples were then dried in an electric drying oven at 105 °C overnight.

3. Products Analyses

3.1. Biochar pH determination

The pH of each biochar sample was performed by placing a 1-gram aliquot of each sample in 10 mL of Millipore water in 20 mL screw-top flasks. The samples were then shaken for 1 hour at 110 rpm at room temperature. The pH of the resultant slurry was then measured

with a glass electrode pH meter. This assay was performed in duplicate.

A second pH measurement was carried out in order to ensure that no excess H_2O_2 was present in the treated biochar samples, and that the measured pH of the treated samples was due to the oxygenation of the biochar itself. The full details of this procedure are as follows: Samples of untreated biochar and biochar treated with 30% H_2O_2 solution were measured for pH as described above. These samples were then transferred to 50 mL centrifuge tubes and then centrifuged at 2000 rpm (973 rcf) for 10 minutes in a Beckman Coulter Avanti® J-26 XP centrifuge using a JS-5.3 rotor. The supernatant was then discarded and 40mL of fresh Millipore water was added to resuspend the biochar samples. These samples were then shaken for 24 hours at 110 rpm, after which they were centrifuged again using the same methods as above. The supernatant again was discarded and this time 10 mL of Millipore water was added. The samples were then shaken for another hour at 110 rpm and the resultant pH of the biochar slurry was again measured. This process was then repeated for another iteration of centrifugation, the addition of 40 mL of Millipore water, and shaking for another 24 hours at 110 rpm, and the pH was measured of the sample as described above.

3.2. Biochar cation exchange capacity measurement

CEC measurements were carried out according to a modified AOAC method 973.09 (Rippy and Nelson, 2007), as follows: 0.5 gram aliquots of biochar samples were placed into 125-mL Erlenmeyer flasks, to which 50 mL of 0.5M HCl solution was added. These samples were then shaken at 110 rpm for 2 hours. The samples were then filtered and rinsed with 100 mL aliquots of Millipore water until the filtrate showed no signs of precipitate when several drops of dilute (0.028M) AgNO_3 solution were added. The precipitate in this case exhibited in

solution as a cloudy, white substance. The filtrate was then discarded and the washed biochar and filter paper (Fisherbrand P8) were then transferred to a clean 125 mL Erlenmeyer flask. A total of 50 mL of with 0.5M Ba(OAc)₂ was added to each flask. The samples were then shaken again for 1 hour, filtered, and washed with 3 x100mL portions of Millipore water. The biochar was discarded and the filtrate titrated with 0.1N NaOH solution using phenolphthalein as an indicator until first pink appeared. This measurement was repeated 6 times for each sample in order to reduce error. The CEC was then calculated according to the following equation:

$$\frac{cmol}{Kg\ biochar} = \frac{mL \times molarity\ NaOH \times 100}{gram\ sample}$$

3.3. Biochar water field capacity measurement

Biochar field water-retention capacity was measured gravimetrically for each sample in duplicate in the method outlined in reference (Kinney et al., 2012). Between 250-400 mg of each biochar sample was first dried overnight at 105 °C, and then subsequently placed into 50-mL centrifuge tubes. To each flask roughly 30 grams of Millipore water was added, and the samples were placed on a shaker platform at 110 rpm for 30 minutes. After 30 minutes of shaking had elapsed, the samples were then gravity filtered through Fisher P8 filter paper, and allowed to drain freely for 30 minutes after the last of the sample had been transferred out of the centrifuge tubes. The field capacity was then determined in terms of grams of retained water per gram of dry biochar sample, accounting for mass of water absorbed by the filter paper (Kinney et al., 2012).

3.4. Biochar elemental analysis

Elemental analysis measurements of C, H, and N content were recorded in house utilizing a Thermo scientific Flash 1112 series Elemental Analyzer. All measurements were performed in triplicate. Standard calibration curves of were created using nicotinamide for hydrogen and carbon content and L-aspartic acid for nitrogen content. Oxygen content was determined by difference.

3.5. Biochar methylene blue adsorption assay

In order to measure the effectiveness of removal of an organic dye from solution via treated versus untreated biochars; a methylene blue assay was employed in duplicate. A procedure modified from (Arami-Niya et al., 2012) was used in the same way as reported previously in (Huff et al., 2014). Aliquots of carefully weighed biochar samples of 50 mg were placed into 50 mL centrifuge tubes. To each of the biochar samples, 30 mL of a 20 mg/L solution of methylene blue was added. The samples were then placed onto a shaker platform at 110 rpm, and allowed to shake for 48, to ensure equilibrium between the biochar sample and the dye in solution. After 48 hours had elapsed, the samples were centrifuged at 2000 rpm (973 rcf) in a Beckman Coulter Avanti® J-26 XP centrifuge using a JS-5.3 rotor for 10 minutes. The samples were then carefully removed from the centrifuge and placed upright in order to prevent disturbing any particulate back into solution. A portion of each sample solution was then placed into a quartz cuvette and absorbance was measured at 665 nm in a Cary 5000 UV-Vis spectrophotometer. The amount of methylene blue adsorbed was calculated according to a previously made 5 point calibration curve and the following equation (Arami-Niya et al., 2012).

$$Q_e = \frac{(C_o - C_e) V}{w} \quad (1)$$

Q_e is the amount of methylene blue removed from solution as reported in mg/g biochar added, C_o and C_e are the initial and equilibrium concentrations (mg/L), respectively, V is the volume of solution used, and W is the grams of biochar used (Huff et al., 2014).

3.6. Biochar FTIR-ATR spectroscopy

For Fourier transformed infrared resonance - attenuated total reflection (FTIR-ATR) spectroscopy, finely ground biochar samples were placed into a ZnSe sample trough. Spectra were then collected using a Shimadzu IRPrestige-21 FTIR spectrometer for 256 scans over a range of 750-4000 cm^{-1} and a resolution of 4 cm^{-1} .

4. Results and Discussion

4.1. Effect of hydrogen peroxide treatment on biochar revealed by FTIR-ATR analysis

FTIR-ATR analysis revealed the changes in the functionality of the biochar samples with respect to treatment with H_2O_2 , as shown in Figure 6. The primary changes occurred at 1585 cm^{-1} , 1315 cm^{-1} , and 775 cm^{-1} between the treated and untreated samples. The peak at 1585 cm^{-1} correlates with the C=C stretching of the aromatic carbons of the sample. Treatment with H_2O_2 caused the peak (C=C) at 1585 cm^{-1} to diminish with respect to the untreated sample, indicating that some of the aromatic carbon content of the sample is being altered. The peaks at 1315 cm^{-1} and 1700 cm^{-1} correspond to carboxylic acid functionality, and were increased with H_2O_2 treatment. There was also an increase of peak intensity at 775 cm^{-1} with H_2O_2 treatment of the samples, which corresponds to an increase in C-H stretching, possibly due to conversion from aromatic C=C ring structures (Wang and Griffiths, 1985).

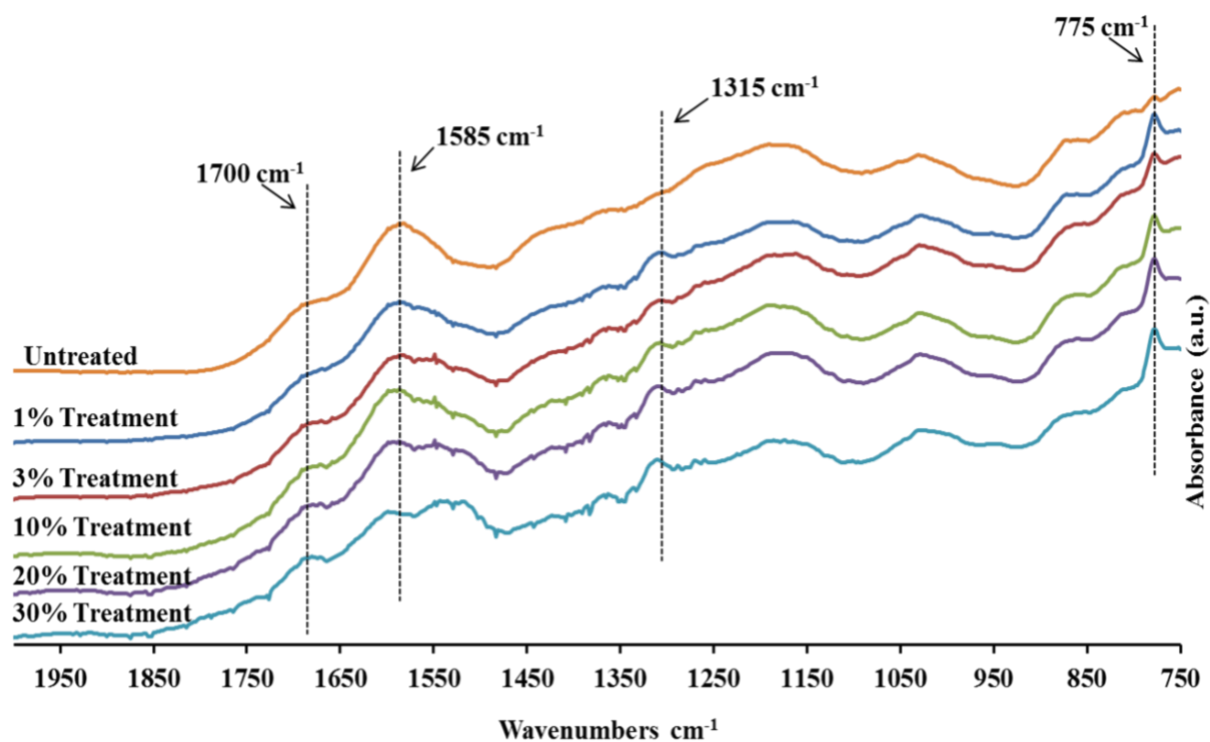


Fig 6. Stacked FTIR-ATR spectra of biochar samples treated with 0 (untreated) to 30% H_2O_2 .

4.2. Elemental analysis results

The elemental analysis of the biochar samples shows that no significant changes occur within the bulk composition of the biochar samples when treated with H_2O_2 , as shown in Table 5. In all samples, the carbon content was measured to be roughly 72%, the hydrogen content roughly 4%, and the nitrogen content was less than 0.5% by mass of each sample. Oxygen content, as calculated by difference, is roughly 25% for all samples. The lack of significant alterations in the bulk composition of the biochar samples demonstrated the inherent stability of biochar even in a highly oxidative environment such as in H_2O_2 solutions. This result is consistent with a previous study that the biochar is predicted to be stable in soil for long periods of time, on a scale of thousands of years (Kuzuyakov et al., 2014). As shown above, the FTIR reveals certain functional changes, and shows an increase in oxygen functionality of biochars treated with H_2O_2 . However, through elemental analysis, it is revealed that these modifications of biochar brought about by H_2O_2 treatment are of minor scale overall, and are localized primarily on the biochar surface. The long term stability of biochar is thereby unlikely compromised by the treatment of H_2O_2 , but rather retained, while the surface of the biochar is altered with respect to oxygen functionality.

Table 5. Elemental analysis of H₂O₂-treated and untreated biochar samples by percentage of C, H, N and balance by mass.

Treatment (% H ₂ O ₂)	C (wt %)	H (wt %)	N (wt %)	Balance (wt %)
1	72.59 ± 1.62	3.63 ± 0.17	< 0.5	23.78
3	71.38 ± 1.22	3.61 ± 0.04	< 0.5	25.01
10	68.73 ± 1.16	3.32 ± 0.38	< 0.5	27.95
20	72.18 ± 0.43	3.83 ± 0.10	< 0.5	23.99
30	71.43 ± 1.70	3.94 ± 0.12	< 0.5	24.63
0 (Untreated)	72.59 ± 0.17	3.86 ± 0.01	< 0.5	23.55

4.3. Biochar field water-retention capacity property

The field capacity of the biochar samples was measured in order to evaluate the water retention capability of the samples. Table 6 shows the relative amounts of water in grams retained per gram of biochar sample. Overall, there is almost no significant difference between the treated and untreated biochar samples in regard to field capacity, with no apparent dependence on the concentration of H₂O₂ used in treatment. Recently, it has been reported that application of biochar as a soil amendment may lead to a substantial relative increases (from 3.2% to 45%) in available soil water content compared to control soils (Baronti et al., 2014). According to the results in Table 6, the hydrogen peroxide treatment did not significantly alter the field water-retention capacity. While it is expected that with the addition of carboxyl groups as indicated by the pH assay as well as the FTIR spectra that the biochar samples would become more hydrophilic, it appears that the changes due to H₂O₂ treatment occurred mostly on the surface of the biochar samples, and therefore have little effect on a bulk property such as biochar pore sizes and surface areas in relation to field capacity.

Table 6. Assay results of H₂O₂-treated and untreated biochar samples for CEC (cmol/ Kg biochar), Field Capacity (grams water retained per gram biochar), pH, and Methylene blue adsorption (mg dye adsorbed per gram biochar).

Treatment (% H ₂ O ₂)	pH	CEC (cmol/Kg)	Methylene Blue Adsorption (mg/g)	Field Capacity (g H ₂ O/g biochar)
(Untreated)	7.16 ± 0.04	17.95 ± 3.53	7.14 ± 0.28	4.69 ± 0.09
1	7.14 ± 0.02	23.75 ± 5.12	7.71 ± 0.33	4.77 ± 0.44
3	7.05 ± 0.01	23.30 ± 5.09	7.41 ± 0.38	4.33 ± 0.76
10	6.70 ± 0.06	25.58 ± 5.40	6.56 ± 0.34	4.24 ± 0.57
20	6.34 ± 0.04	25.43 ± 4.13	6.57 ± 0.07	4.62 ± 0.45
30	5.66 ± 0.03	31.37 ± 6.17	5.50 ± 0.37	4.76 ± 0.35

4.4. Effect of hydrogen peroxide treatment on biochar cation exchange capacity

The assay result showed that the change in biochar CEC value was dependent on the concentration of the H₂O₂ solution used in the treatment. Column 2 of Table 6 shows the increase in CEC (in units of cmol/Kg biochar) from 17.95 ± 3.53 for untreated biochar, to 31.37 ± 6.17 for biochar treated with 30% H₂O₂ (w/w) solution. This increase in CEC capacity is apparently due to the increase in oxygen-containing functional groups which are created by the hydrogen peroxide treatment on biochar surface, which are readily accessible for exchanging cations in solution. The treatment with higher concentration of H₂O₂ appears correlated to a greater degree of oxygenation of biochar, primarily exhibited as carboxyl groups. Carboxyl

groups are slightly acidic in nature, and in basic or neutral aqueous solutions carry an overall negative charge that is capable of favorable interactions with cations. This increase in CEC of the biochar samples is important in the consideration of biochar as a soil amendment in order to increase the overall CEC of soils for better retention of plant soil nutrients.

4.5. Effect of hydrogen peroxide treatment on biochar pH

As shown in Table 6, the pH of the biochar samples decrease with treatment of increasing H₂O₂ concentration. This is believed to be due to an increasing amount of carboxyl groups created by the H₂O₂ treatment on the biochar surface, which are inherently weakly acidic. The biochar pH dropped from 7.16 ± 0.04 of the untreated sample to $\text{pH } 5.66 \pm 0.03$ for the 30% H₂O₂ treated sample. The change in pH brought about by H₂O₂ treatment appears to be a function of the H₂O₂ concentration during the treatment.

In order to ensure that this measured pH change was the result of functional changes, and simply not residual H₂O₂ left over from treatment, a further pH study, as outlined in the SI, was carried out on the biochar sample treated with the 30% solution of H₂O₂. It was found that even with successive rinses, which should have removed any residual H₂O₂, the pH of the treated biochar did not change. The initial pH values of the secondary pH study were 5.60 ± 0.05 , followed by a measurement of 5.57 ± 0.03 after a 40 mL rinse with Millipore water and 24 hours of shaking at 110 rpm, and finally a measurement of 5.54 ± 0.02 after yet another 40-mL rinse with Millipore water and 48 hours total of shaking at 110 rpm. This additional pH study also showed that the added functional changes on the biochar surfaces remain stable in liquid solution as demonstrated during the assay, an important factor when considering the function of treated biochars in their use for soil amendments.

4.6. Methylene blue adsorption

Methylene blue is widely used to evaluate the capacity of dye removal of biochar, activated carbons, and other adsorbent materials (Rafatullah et al., 2010). The dye molecule of methylene blue itself is aromatic in nature and non-polar, and contains a positively charged amine group. As previously published, the capacity of biochar for methylene blue adsorption does not increase concurrently with increasing CEC of biochar samples (Huff et al., 2014). Table 6 shows (in units of mg of dye adsorbed per gram of biochar) that the methylene blue adsorption capacity is highest in the untreated and in low (1-3%) concentration H₂O₂ treated biochars. The highest dye removal capacity was recorded for the 1% treated sample at 7.71 ± 0.33 mg/g, and the lowest dye removal capacity was that of the 30% treated sample at 5.50 ± 0.37 . The general trend is that with the higher H₂O₂ concentration treatments the lower the methylene blue adsorption capacity becomes. This trend correlates well when considering the mechanism by which methylene blue is adsorbed from solution onto biochar; namely, the π - π interactions between the dye and the biochar (Radovic et al., 2001; Valdes et al., 2002). With the addition of carboxyl groups onto the surface of the biochar sample by the hydrogen peroxide treatment, the electron density is removed from the π band of the carbon of the biochar, thereby weakening the overall dispersion forces between the methylene blue and the surface of the biochar sample (Valdes et al., 2002).

5. Conclusions

Biochar treated with H_2O_2 showed an increase in CEC over the untreated sample. This increase in CEC can be attributed to an increase in the presence of acidic oxygen functional groups on the surface of the biochar materials, as additionally evidenced by FTIR and the pH assay reported above. Furthermore, H_2O_2 treatment caused an overall drop in biochar's capacity for the removal of methylene blue from solution, likely resulting from the weakening of π - π dispersive forces brought about by the introduction of oxygen functionality which disrupts the overall aromatic structure of the biochar sample. This trend points toward the need of further understanding of the end purpose of the biochar subjected to for partial oxygenation treatments, as it must be noted that while some attributes (such as CEC) are positively affected, others (methylene blue removal capacity) are reduced. As previously reported, for biochar materials without any special surface treatment, an overall increase in the O:C ratio could indicate that the biochar may have higher cation exchange capacity and lower long term stability (Huff et al., 2014; Lee et al., 2010; Spokas, 2010). In the case of the biochars treated with hydrogen peroxide in this study, it appears that the samples were only modified superficially on biochar surfaces that can be detected by cation exchange capacity measurement, but can hardly be measured by elemental analysis of the bulk biochar material property; These results show that the partial oxygenation of biochar through H_2O_2 treatment yield a biochar with higher CEC without changing the bulk property of the biochar, which may have implication in fundamental understanding and development of more desirable biochar materials for their potential application as a soil amendment (Dai et al.; 2013; Novak and Busscher, 2013; Novak et al., 2014; Windeatt et al., 2014; Zha et al., 2015; Zhang et al., 2015; Zhao et al., 2014).

CHAPTER IV

SURFACE OXYGENATION OF BIOCHAR THROUGH OZONIZATION FOR DRAMATICALLY ENHANCING CATION EXCHANGE CAPACITY

Preface:

The content of this chapter was published in the Journal Bioresources and Bioprocessing in 2018. The full citation can be found below. The publication has been modified in order to integrate the supporting information relevant to the publication into chapter.

Huff, M. D., Marshall, S., Saeed, H. A., & Lee, J. W. (2018). Surface oxygenation of biochar through ozonization for dramatically enhancing cation exchange capacity. Journal of Bioresources and Bioprocessing, 5, 1-9.

1. Introduction

The world currently faces a systemic food, energy and water systems-associated problem of decreasing soil fertility with decreased soil organic carbon content and increasing CO₂ emissions and global-climate change. Recently, biochar has garnered much attention due to its potential usage as a soil amendment, carbon sequestration agent, and as an inexpensive analogue to activated carbon for wastewater treatment (Sohi, Krull et al. 2010; Regmi, Garcia Moscoso et al. 2012; Lee and Day 2013; Lee, Hawkins et al. 2013; Mohan, Sarswat et al. 2014). As a soil amendment, the use of biochar with high CEC has been shown to improve soil property such as the ability to retain soil nutrients, which is an important attribute for agronomic purposes in that it reduces the nutrient leaching. However, it must be understood that not all biochars behave in a similar manner when used as a soil amendment, as it has been shown that while some biochars will increase crop yields, other biochars either have no effect, or a negative effect on crop yields

(Jeffery, Verheijen et al. 2011; Spokas, Cantrell et al. 2012; Novak, Ippolito et al. 2016). The conventional biochar material in the current market typically has quite low cation exchange capacity (CEC), a key property that is central to help retain soil nutrients and water. Better biochar materials with higher CEC are needed to achieve the mission of biochar soil amendment and carbon sequestration for agricultural and environmental sustainability on Earth (Lee, Hawkins et al. 2010; Lee, Hawkins et al. 2016).

Technically, this is due to a number of factors, given that biochars are generated from a wide range of materials, temperatures, and methods, therefore leading to biochars of widely varying characteristics such as pH, CEC, surface area, and ash content (Lim, Spokas et al. 2016). These characteristics ultimately determine the usefulness of biochar in a given application such as soil amendment and/or wastewater treatment. Currently most of the biochar materials are produced by pyrolysis, but additional methods such as hydrothermal conversion have also been explored. Pyrolysis can generally be divided into three main categories: slow pyrolysis, fast pyrolysis, and gasification. Slow pyrolysis generally has longer retention times (≥ 30 Minutes) when compared to fast pyrolysis and gasification. Slow pyrolysis tends to generate more biochar from biomass and less bio-oil and syngas products when compared to fast pyrolysis and gasification due to the use of lower treatment temperatures (E, Klaus et al. 2009). Higher pyrolysis temperatures like those used for gasification ($>700^{\circ}\text{C}$) tend to create more gaseous products typically resulting in a low biochar yield with lower biochar CEC. Any innovative approach that can more effectively produce better biochar materials with higher CEC value may be helpful to achieving the biochar mission towards sustainability on Earth (Lee, Kidder et al. 2010; Woolf, Amonette et al. 2010).

In order to ensure biochar efficacy, the use of “designer biochars” has been proposed (Day, Evans et al. 2005; Novak and Busscher 2013). Since many of the conventional biochar production methods can yield products with quite low CEC values, the development of technologies to increase CEC is needed. Industrially, post-production processing techniques for biochar usually involve treatments with H_2SO_4 or KOH , which can be unfavorable on a large scale due to the generation of unwanted by-products.

It has been shown previously that there is a strong correlation between the O:C ratio of a biochar sample and its CEC, which is due to the native negative charge on the aforementioned oxygen functional groups which electrostatically attract cations from solution. (Huff, Kumar et al. 2014) (Lee, Kidder et al. 2010) While a high O:C ratio is desirable for high CEC when using biochar as a soil amendment, it must also be understood that the higher the O:C ratio is, the shorter the overall half-life of the biochar. Biochars with O:C ratios higher than 0.2 have half-lives less than 1000 years (Spokas 2010). Even higher O:C ratios drop the expected half-lives precipitously to <100 years for an O:C ratio of ≥ 0.6 . Therefore, an ideally designed biochar for use as both a soil amendment and carbon sequestration agent would need to intelligently enhance the O:C ratio only on the surface of biochar, giving a higher CEC, while still maintaining the poly-aromaticity (preferably lower O:C ratio) of the biochar hard core for long-term stability.

Currently, the limited CEC value of the conventional biochar materials is one of the limiting factors that impedes the success for widespread commercial biochar applications. In this paper, we report an innovative biochar ozonization process as a post-production surface-oxygenation treatment (Fig. 7) that can dramatically enhance biochar CEC value, which is a key property central to better retain nutrients in soil amendment and to remove certain pollutants in water-filtration sciences and technology application (Lee 2017).

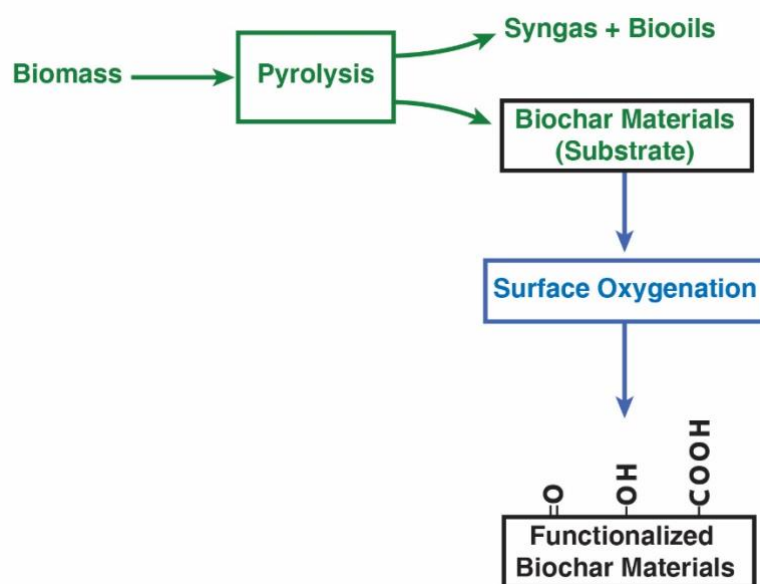


Fig.7 Process schematic showing post-production surface-oxygenation treatment (e.g., ozonization) to create oxygen-containing functional groups on the biochar surface.

2. Materials and methods

2.1 Materials

The soil reference sample used in this study was provided by Dr. Charles Garten of Oak Ridge National Laboratory as reported previously (Huff et al., 2014). The sample was autoclaved for 30 minutes at 120° C prior to use in analyses.

2.2. Biochar synthesis

The biochar used in this study was synthesized from biomass sourced from Old Dominion University. A fresh limb from an eastern shore pine tree was acquired on campus and cut to a usable size of 1 cm thickness and 3-5 cm in length. Before being introduced to the pyrolysis reactor the biomass was dried in an electric oven at 105° C. The biomass was then placed into a 500 mL hastelloy autoclave parr reactor and heated to 400° C. Once reaching 400°

C the reactor was held at that temperature for 30 minutes. After 30 minutes had elapsed, the reactor was cooled and the biochar collected and weighed. Before further analysis the biochar sample was rinsed and filtered with 200 mL portions of Millipore water 3 times and dried again in an electric oven at 105° C. The biochar was then thoroughly ground through a 106 µm sieve (U.S.A Standard Testing Sieve NO. 140).

2.3. Ozone treatment

Biochar samples in 1 g aliquots were introduced into a specialized glass tube reactor. The gas inlet of the reactor was connected with an ozone-compatible gas tube to a Welsbach T series ozone generator that was connected to a compressed O₂ gas tank with a pressure regulator and a needle valve/gas flow meter that controls the gas flow rate. The reactor and the in-line ozone generator chamber were flushed with a flow of O₂ for five minutes at a rate of 3 L/min at ambient temperature before the ozone generator was turned on. After the five minutes of O₂ flow time had elapsed, the Welsbach T series ozone generator was then turned on at a voltage of 115V to generate ozone from O₂ in-line at a shell pressure of 8 psi. Depending on the experiment, the biochar was exposed to ozone for either 30, 60, or 90 minutes. After ozone treatments, the biochar was then rinsed out of the reactor with 3 X 100 mL portions of Millipore water. The samples were then dried in an electric oven at 105° C prior to use for further analysis.

2.4. pH determination

Biochar pH was determined in 6 replicates (n=6) by placing 1.0 grams of biochar into a 20 mL flask and adding 10mL Millipore water to each flask. The resultant biochar slurry was then shaken on an *innova 2300* platform shaker for 1 hour at 100 rpm. After shaking, the pH of each sample was taken using a Thermo Scientific pH probe.

2.5. Cation exchange capacity (CEC) measurement

CEC measurements were performed in 6 replicates (n=6) following a modified protocol from AOAC method 973.09 (Rippy and Nelson, 2007). Briefly, 0.5 g samples of biochar were placed in 125 mL Erlenmeyer flasks each to which 50 mL of a 0.5 M HCl solution was added. The flasks were then shaken at 110 rpm on an *Innova 2300* shaker for 2 hours. Using a Buchner funnel filtration system and Whatman™ GF/F 70-mm glass microfiber filters, the samples were filtered and washed with 100 mL portions of water until the filtrate showed no precipitate with the addition of AgNO₃ solution. The biochar samples were then transferred into clean 125 mL Erlenmeyer flasks and a total of 50 mL of a 0.5M Ba(OAc)₂ solution was added to each. These flasks were then again transferred to an *Innova 2300* shaker and shaken for 1 hour. After the hour had elapsed the samples were filtered in the manner mentioned above, and washed with 3 X 100 mL portions of water. The biochar samples were then discarded and the filtrate was titrated with a 0.1M NaOH solution until an endpoint indicated with phenolphthalein was reached. The full calculation for the CEC can be found in the supplemental information provided in (Huff and Lee, 2016).

2.6. *Water field capacity measurement*

The water-retention capacity of each biochar sample was measured in duplicate gravimetrically following the previously established protocol (Kinney et al. 2012). All biochar samples were first dried thoroughly overnight at 105° C. Aliquots of 400-500 mg of each dried biochar sample were weighed and placed into 50 mL centrifuge tubes. To each tube, 30 grams of Millipore water was added and the samples were then shaken at 110 rpm for 30 minutes. Following the 30 minutes of shaking the samples were then filtered through Whatman™ GF/F 70-mm glass microfiber filters with glass funnels. The samples were allowed to drain freely for 30 minutes after all of the sample had been transferred from the centrifuge tubes onto the glass microfiber filters. Glass evaporating dishes were used as covers over each of the filters to limit error brought about by evaporation loss. The field capacity was calculated as the amount of water in grams retained per gram of dry biochar, while also accounting for the mass of the water on the filter paper.

2.7. *Methylene blue adsorption assay*

Methylene blue adsorption capacity of the biochar samples were assayed in duplicate using a modified procedure as reported previously (Arami-Niya et al., 2011 and Huff et al., 2014). Briefly, around 50 mg of each biochar samples was weighed carefully and placed into a 50 mL centrifuge tube. To each of these centrifuge tubes, 30 mL of a 20 mg/L solution of methylene blue in water was added. The samples were then transferred to an *Innova 2300* shaker platform and shaken at 100 rpm for 48 hours. After 48 hours had elapsed the samples were placed into a Beckman Avanti® J-26 XP centrifuge and spun down at 2000 rpm (973 rcf) for 10 minutes utilizing a JS 5.3 rotor in order to remove particulate. The samples were then analyzed on a UV-Vis spectrometer and the amount of methylene blue adsorbed was recorded as mg dye

removed per gram of biochar according to the following equation as previously reported (Arami-Niya et al., 2011):

$$(1) \quad Q_e = \frac{(C_o - C_e)V}{W}$$

Herein, Q_e is the amount of methylene blue removed from solution with biochar reported in mg dye/g biochar. C_o and C_e are the initial and equilibrium amounts, respectively. V is the total volume of dye solution used, and W is the mass of biochar used in grams (Huff et al., 2014).

2.8. Metal adsorption assays

All batch adsorption experiments were performed in triplicate. After drying overnight in an electric oven at 105° C, 50 mg aliquots of untreated and treated biochar samples were carefully transferred into 50mL centrifuge tubes. To each of the centrifuge tubes, 30 mL of metal ion solution was added. This mixture was then transferred to a shaker platform and shaken at 110 rpm for 24 hours at room temperature. After the 24 hours had elapsed, the pH of each solution was measure and adjusted to between pH 4.5-5.5 with 0.5M HCl or 0.1M NaOH in order to avoid precipitation of the metal species from solution. The centrifuge tubes were then transferred back onto the shaker platform for another 24 hours, using the same parameters mentioned above. After 48 hours of shaking in total, the pH was measured again and adjusted to between pH values of 4.5-5.5 as needed. The centrifuge tubes were then shaken for 1 additional hour to ensure equilibrium. After the final hour of shaking, the centrifuge tubes were then placed into a Beckman Avanti centrifuge utilizing a JS 5.3 rotor and centrifuged for 10 minutes at 3000 rpm. The metal ion concentration remaining in the filtrate was then measured using a Shimadzu 7000-AA analyzer with a flame ionization source.

2.9. Elemental analysis

Elemental analysis was performed using a Thermo scientific Flash 1112 series Elemental Analyzer to determine C, H, and N content of the biochar samples. Measurements were performed in triplicate, and oxygen content was determined by difference.

2.10. FTIR-ATR spectroscopy

Biochar samples were analyzed via Fourier Transformed infrared resonance- attenuated total reflection spectroscopy utilizing a Shimadzu IRPrestige-21 FTIR spectrometer. Spectra were collected at a resolution of 4 cm^{-1} over 256 scans and a range of $750\text{-}4000\text{ cm}^{-1}$.

2.11. Gaseous products analysis

A mass spectrometer consisting of a quadrupole probe known as the Universal Gas Analyzer (UGA) was used to characterize the components of the gas mixture from the reactor gas outlet, which is at, or below, atmospheric pressure. The UGA can identify the different constituent molecular species in the gas, their relative abundances and track this information in real time measurement (Fast response time $<0.2\text{ s}$). It analyzes the sample providing partial pressure vs mass data. The UGA was run in the real time mode for in-line monitoring of the ozone generation, the ozone consumption and other gaseous mixture during the treatment process. Pressure versus time mode was run in which each gaseous partial pressure was acquired directly from the UGA by individually querying the partial pressure for their appropriate masses. This was done for all the selected masses of gaseous species using the present scan schedule as a trigger.

2.12. Thermal imaging of biochar ozonization

Temperature changes during ozone treatment of biochar were measured using a FLIR E60 thermal imaging camera. In order to verify temperature changes during the ozonization reaction, a larger amount of biochar (50 grams) was used under the same conditions as written above with a 10 minute treatment time with ozone.

2.13. Raman spectroscopy

Raman spectra were acquired using an in-house designed spectrometer featuring an 852-nm DBR GaAs diode laser run in constant current mode. The spectrometer has been described in detail previously (Cooper et al., 2013a; Cooper et al., 2013b; Cooper et al 2014). The excitation wavelength was adjusted 32 times by setting the temperature of the laser to pre-determined values that provide 1 cm^{-1} spacing between each shift. Each single spectrum is composed of 250 co-added spectra each collected for 850 ms. The spectra were analyzed using the moving-window sequentially shifted excitation (MW-SSE) algorithm in order to remove the intense fluorescence background. The algorithm was run using a 32 cm^{-1} window, with each window undergoing 50,000 iterations. No additional filtering or baseline corrections were performed.

3. Results

3.1. Effect of ozone treatment on biochar pH

Table 7 shows the change in pH of the biochar samples brought about by treatment with ozone. Overall there is a dramatic decrease in the pH of the biochar samples from 7.30 ± 0.39 of untreated biochar to 5.28 ± 0.33 of the sample treated with 90 minutes of ozone. This sharp decrease in pH is believed to be brought about by the addition of acidic functional groups, primarily carboxyl groups on the surface of the biochar. The trend in pH values shows that there

is a relationship between treatment time and increasing acidity of the biochar samples. This drop in pH is an important characteristic when considering using biochar as a soil amendment, and that through the use of ozone treatments; it is possible to “tune” biochar pH to a desired value.

Table 7

Summary data for pH, CEC (cmol/kg), Methylene blue adsorption (mg dye adsorbed/ gram biochar), and Field Capacity Measurements (g H₂O/g biochar)

Sample	pH	CEC (cmol/kg)	Methylene Blue Adsorption (mg/g)	Field Capacity (g H ₂ O /g biochar)
Untreated	7.30 ± 0.39	15.39 ± 1.59	1.79 ± 0.18	4.88 ± 0.02
30 Min O ₃	5.46 ± 0.40	30.26 ± 3.23	9.22 ± 0.18	3.63 ± 0.02
60 Min O ₃	5.33 ± 0.28	31.03 ± 2.44	9.45 ± 0.07	2.92 ± 0.21
90 Min O ₃	5.28 ± 0.33	32.69 ± 2.51	9.35 ± 0.04	3.38 ± 0.08
Soil Ref.	N/A	12.75 ± 1.01	N/A	2.03 ± 0.40

3.2. Biochar cation exchange capacity

As shown in Table 7, the ozone treatment significantly increased the CEC value of biochar. The untreated biochar sample had a CEC of 15.39 ± 1.59, and the sample treated with 90 minutes of ozone had a value of 32.69 ± 2.51 (in units of cmol/kg biochar). Table 7 also lists the CEC value of a soil reference sample of 13.18 ± 0.96. From this, it is clear that even untreated biochar has a higher CEC of the reference soil sample, and treated samples have CEC values more than twice of that of the reference soil sample. Statistically, there is only a small difference between the 30, 60, and 90 minute ozone treated samples, which is potentially due to a saturation of the sites available for alteration by ozone treatment. Specifically, cation exchange

capacity correlates to the available oxygen function groups, predominately carboxylic acid groups which carry a negative charge in basic and neutral solutions, making them electrostatically attracted to cations. This finding is well in line with previous reports that CEC correlates strongly with increasing oxygen functionality in biochar (Lee et al., 2010; Huff et al., 2014; Huff and Lee, 2016; Carrier et al., 2012). This increase of oxygen functionality in the biochar samples is also supported by the mechanism proposed previously by Gómez-Serrano, et al., which states: The electrophilic ozonolysis of carbon (C=C) double bonds in olefinic structures is expected to occur in a process involving three steps: (1) 1,3-dipolar addition of ozone to the double bond to give an unstable primary ozonide; (2) decomposition of the primary ozonide by a 1,3-dipolar reversion to yield a carbonyl compound and a carbonyl oxide; (3) the carbonyl oxide may give a normal ozonide, dimerizes to aldehyde or ketone diperoxides, or polymerizes to give polymeric peroxides or ozonides (Gomez-Serrano et al., 2002).

3.3. Water-retention field capacity

Field capacity measurements were employed to evaluate the water-retention properties of biochar and to analyze the effects that ozone treatment would have on the biochar samples. Table 7 shows the relative amounts of water retained by each biochar sample as well as a soil reference in units of g water retained/ g biochar. In general, there is a slight decrease in water retention after ozone treatment on the biochar samples. There is no clear correlation between treatment time and decrease in water retention. As with the CEC measurement, all of the biochar samples have higher values of water retention than the soil reference sample.

3.4. Biochar methylene blue adsorption

Methylene blue adsorption capacity was measured to evaluate the biochar samples' viability for dye-contaminant removal in water systems. As shown in Table 7, there is a dramatic increase in methylene blue removal capacity brought about by ozone treatment, with the untreated biochar sample only removing 1.79 ± 0.18 mg dye/g biochar while the 90 minute ozone treated sample removed 9.35 ± 0.04 . This significant increase shows the usefulness of ozone treatment when considering biochar amendment for use in contaminated water systems. It is believed that the increase in methylene blue adsorption capacity is due to the increase of oxygen functionality on the surface of the biochar, which makes the biochar overall more negatively charged. Methylene blue is natively positively charged in solution, and therefore is more electrostatically attracted to biochar that has been treated with ozone.

3.4. Metal adsorption assays

The effect of ozone treatment of biochar's effectiveness for metal removal is shown below in Tables 8 and 9. Overall, there is an increase in effectiveness with ozone treatment, although the treatment that showed the greatest improvement in terms of duration varied per metal species. Ni (II), Cd (II), Pb (II), and Zn (II) were all removed in the highest amount utilizing the biochar treated with 90 minutes of ozone, while Mg (II) and Cu (II), were removed most effectively with the biochar treated with 60 minutes of ozone. A similar effect was noticed by Zuo et. al., wherein biochar treated with 20% H_2O_2 was more effective at the removal of copper than biochar treated with 30% H_2O_2 . (Zuo et al., 2016). The non-linear relationship with the increase of metal removal with the duration of ozone treatment suggests that for certain metal species, different treatment times should be utilized. However, it is worth noting that ozone

treatment increased the metal adsorption capacity of the biochar samples above that of the untreated biochar samples for every metal contaminant in this study. The full data set including standard deviations concerning the metal adsorption assays (reported as mg of metal/ per gram biochar and percent values) in this study can be found in Tables 8 and 9.

Table 8 Effect of ozone treatment on metal adsorption values (mg metal/ per gram biochar and standard deviations)

Time (min)	Metal adsorption capacity in mg g ⁻¹ and standard deviations					
	Cu (II)	Ni (II)	Cd (II)	Pb (II)	Zn (II)	Mg (II)
Untreated	1.17 ± 0.08	1.46 ± 0.04	0.61 ± 0.05	16.08 ± 1.18	0.09 ± 0.02	0.02 ± 0.00
30	1.47 ± 0.04	1.80 ± 0.05	0.41 ± 0.05	12.76 ± 0.62	0.16 ± 0.01	0.04 ± 0.00
60	1.73 ± 0.08	1.98 ± 0.11	0.44 ± 0.04	13.09 ± 0.45	0.21 ± 0.02	0.06 ± 0.01
90	1.25 ± 0.13	2.14 ± 0.30	0.83 ± 0.04	16.79 ± 1.51	0.24 ± 0.02	0.01 ± 0.00

Table 9 Effect of ozone treatment on metal adsorption values (percent values and standard deviations)

Time (min)	Metal adsorption capacity percent values and std. deviations					
	Cu (II)	Ni (II)	Cd (II)	Pb (II)	Zn (II)	Mg (II)
Untreated	27.87 ± 1.70	12.34 ± 0.41	34.04 ± 2.73	76.12 ± 5.92	7.68 ± 1.63	3.63 ± 0.14
30	35.22 ± 0.83	15.06 ± 0.33	22.93 ± 2.58	60.35 ± 3.16	13.57 ± 1.24	6.57 ± 0.61
60	41.28 ± 1.87	16.47 ± 0.98	24.17 ± 2.63	62.07 ± 2.59	17.08 ± 1.56	10.29 ± 2.10
90	29.99 ± 3.17	18.04 ± 2.53	46.08 ± 2.16	79.87 ± 7.86	20.30 ± 1.87	1.81 ± 0.82

3.5. Elemental analysis measurement

Elemental analysis measures the bulk composition of the biochar and is useful in determining the degree of change brought about by ozone treatments. Overall, there is not a dramatic change through the use of ozone treatments as shown in Table 10. However, there is a clear drop in carbon content from $73.90\% \pm 0.06$ of the untreated sample to $66.76\% \pm 2.77$ of the 30 minute ozone treated sample. Additionally, it appears to be an increase in oxygen content of the biochar samples as measured by difference, from the untreated (22.78%) to the 30 minute ozone treated sample (30.07%). This data correlates well with the concurrent drop in pH of these samples, as well as the increase in CEC, both owing the change in their properties due to an increase in oxygen functionality. The drop in carbon content across all samples also reveals that during ozone treatments, ozone molecules selectively attack the carbon-carbon double bonds in the biochar, which is also shown in the FT-IR data in Fig. 6. It should be noted that there is not a significant change between the untreated and the 90 minute treated sample in terms of carbon content, owing to the inherent stability of the biochar itself.

Table 10 Results of treated and untreated biochar samples for elemental analysis measured by percentage of C, H, N, and balance.

Sample	% C	% H	% N	Balance
Untreated	73.90 ± 0.06	3.32 ± 0.06	< 0.5	22.78
30 Min O ₃	66.76 ± 2.77	3.17 ± 0.45	< 0.5	30.07
60 Min O ₃	71.70 ± 0.27	3.35 ± 0.07	< 0.5	24.95
90 Min O ₃	71.31 ± 0.30	3.34 ± 0.04	< 0.5	25.35

3.6. FTIR-ATR spectroscopy

The FTIR-ATR spectra as shown in Fig.7 reveal information about the functional group changes brought about by ozone treatment. Two peaks appearing at 1590 cm^{-1} and 1440 cm^{-1} correspond to elastic and inelastic stretching of carbon-carbon double bonds in an aromatic ring structure. These two peaks primarily appear only in the untreated sample, and are greatly reduced in the ozone treated samples, revealing that the ozone selectively reacts with the double bonded carbon throughout the biochar substrate. Furthermore, a peak at 875 cm^{-1} on the untreated sample spectra corresponding to C-H out of plane stretching from an aromatic carbon ring is also greatly reduced with ozone treatment, showing further evidence of the reaction of ozone selectively with carbon-carbon double bonds, although it is possible this could be a reaction of carbonate with ozone as well (Wang and Griffiths, 1985, Reig, et al., 2002).

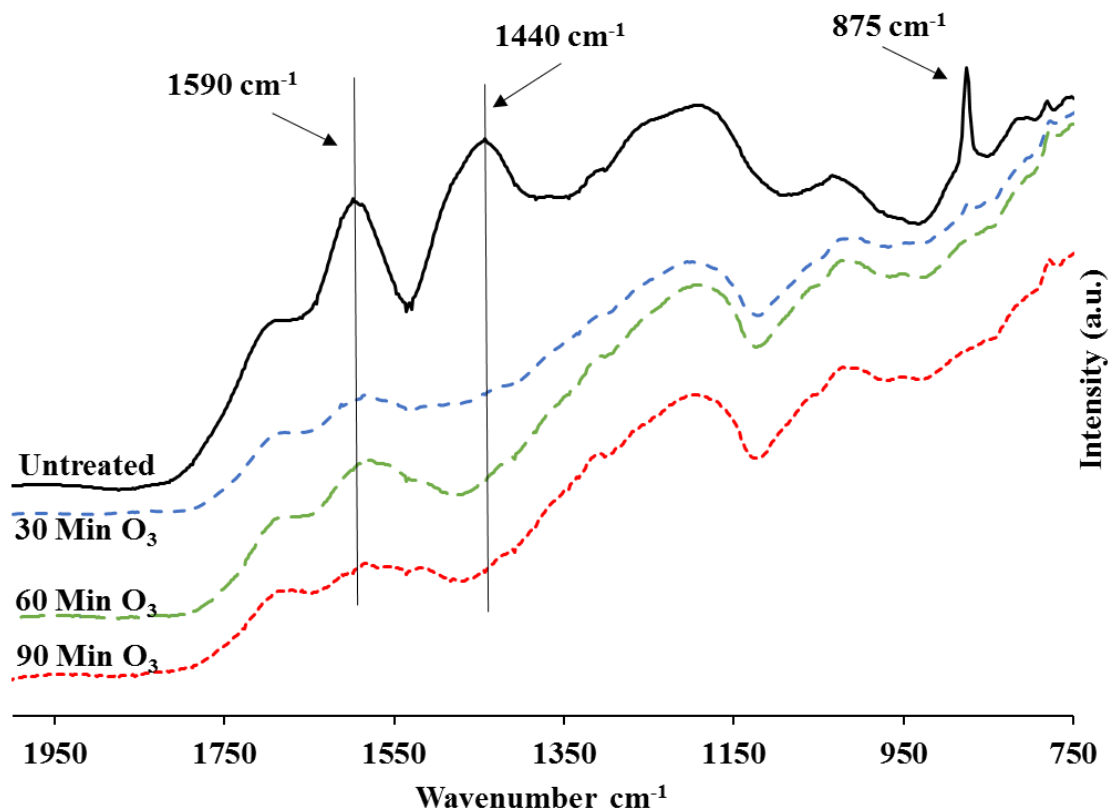


Fig. 8. FTIR-ATR spectra of untreated and ozone treated biochars.

3.7. Gaseous products measurement

Pressure versus time mode was utilized in which each gaseous partial pressure was acquired directly from the UGA by individually querying the partial pressure for their appropriate mass. This was done for all the selected molecular gas masses using the present scan schedule as a trigger. During the ozone treatment of 1 g of biochar, we noticed an increase in the partial pressure of carbon dioxide (P_{CO_2}) from 1.91×10^{-8} torr to 2.2×10^{-8} torr. In order to verify that CO_2 was being produced, a second experiment was performed using 35 grams of biochar to further examine the possible generation of CO_2 during ozone treatment. Therefore, the CO_2 partial pressure in the reactor tail gas was monitored during the reaction of ozone with both 1 gram or 35 grams of biochar. In order to establish a baseline, 10 minutes of atmospheric background were recorded. The UGA measurements were made for each of the following 10 minute intervals: O_2 on (no ozone), ozone on, O_2 on (no ozone), ozone on, O_2 on (no ozone), and lastly a second atmospheric background. If the slight increase in CO_2 partial pressure observed with 1 g of biochar sample was generated from the biochar ozonization chemistry, treating an increased amount (35 grams) of biochar with ozone would lead to an increased CO_2 partial pressure in the reactor tail gas. During the ozone treatment of the 35 grams of biochar, a noticeable increase in the partial pressure of carbon dioxide (P_{CO_2}) from 1.58×10^{-8} torr to 4.01×10^{-8} torr was detected. Full details for this process are shown in figure 8. This confirms that there is certain detectable amount of CO_2 gas produced during the biochar ozone treatment which appears proportional to the amount of the biochar present in the ozonization process.

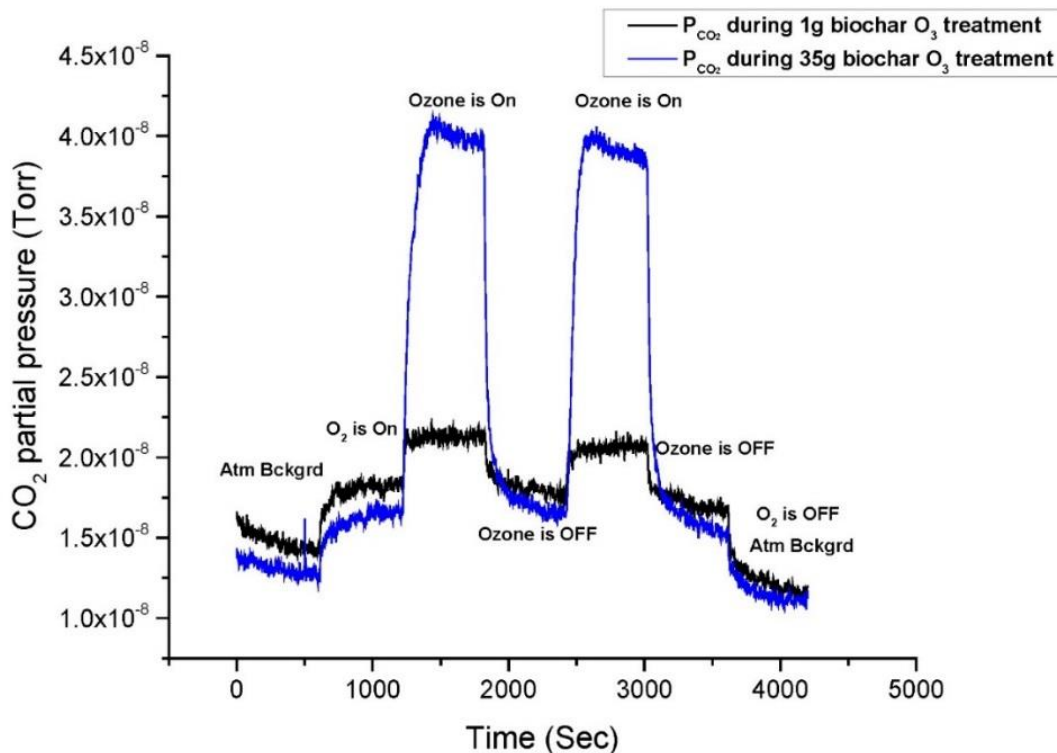


Fig. 9. Partial pressure of CO₂ versus time (sec) during ozone treatment of 1 and 35 gram biochar samples.

3.8. Thermal imaging of biochar during ozonization

Fig. 9 shows the picture in picture (standard image with thermal image overlay) of the biochar ozonization treatment. The central part of Fig. 9 shows the thermal imaging of the tube reactor containing 50 g of biochar and clearly reveals a hot spot where the ozone is being introduced in the reactor, and coming into contact with the biochar, which reveals that the biochar ozonization reaction(s) is exothermic. The reaction was recorded with thermal imaging throughout the duration of the experiment and it was noted that the biochar first began increasing

in temperature primarily closest to where ozone was being introduced. This increase in temperature then spread throughout the biochar sample over the course of the reaction. Fig.9 also shows the peak temperature of the reaction at 90.3° C after 10 minutes of ozone treatment. The biochar and the ozone gas flow all were at room temperature (23° C) at the beginning of the experiment.

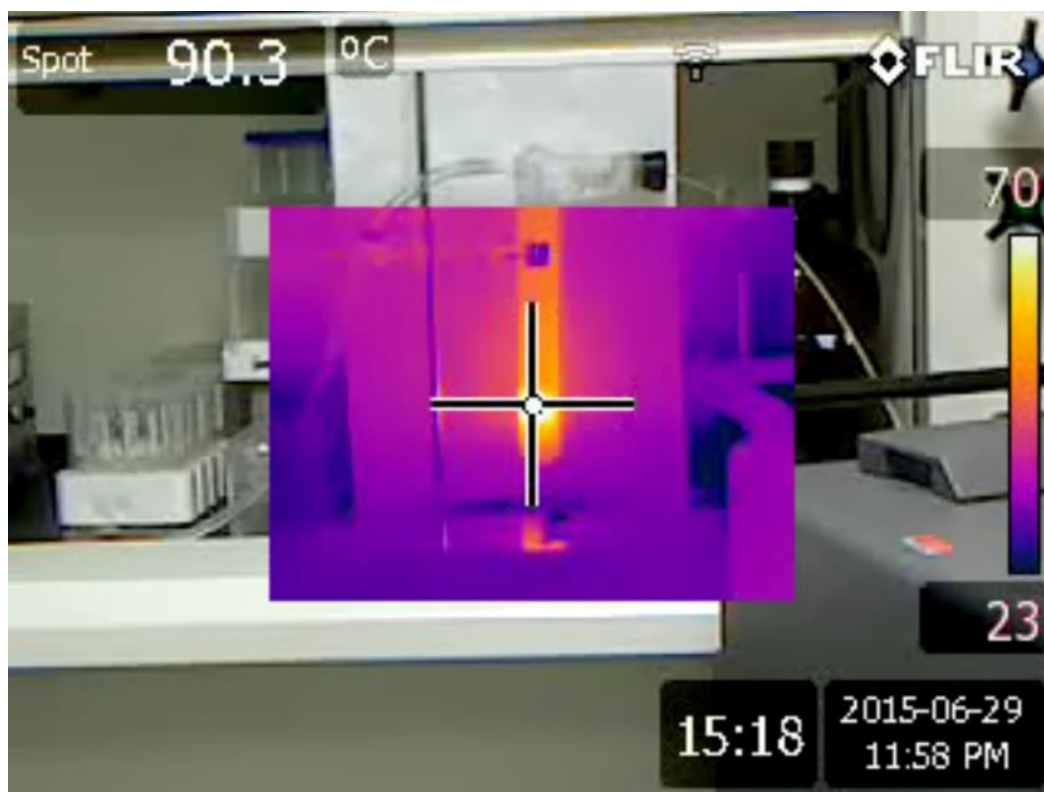


Fig. 10. Picture in picture thermal imaging of the tube reactor during biochar ozonization with its temperature scale (23-70° C) displayed on the far right side. The experiment began with introduction of ozone gas into the reactor containing 50 g of biochar at ambient temperature (23° C). As ozone reacting with biochar, the reactor got warmer. The top left value of 90.3° C denotes the temperature recorded at the biochar reactor hot spot, as pointed by the cursor after 10 minutes of ozone treatment (recording time 15:18).

3.9. Biochar Raman spectroscopy

Fig. 10 shows the Raman spectra for both the untreated biochar sample and the biochar sample treated with 60 minutes of ozone exposure. Both samples share several prominent peaks centered at 1580 cm^{-1} and 1340 cm^{-1} , which correspond to the G and D bands of ordered and disordered graphite, respectively (Zhang et al., 2014). The strong peak at 1450 cm^{-1} , which appears solely in the untreated sample corresponds to olefinic groups within the biochar sample. (Wu et al., 2009) The breakdown of olefins via ozonization in the biochar samples supported clearly in the Raman spectra. A drastic decrease in the peak centered at 1450 cm^{-1} from the untreated to the ozone treated sample corresponds with a reduction of olefinic structures (Wu et al., 2009). Additionally, this spectra also shows that the change of the structure of biochar is primarily due to reactions with olefins rather than aromatic structures, as the peaks centered at 1580 cm^{-1} (ordered graphite) and 1340 cm^{-1} (disordered graphite) are almost completely unchanged when comparing the spectra of untreated and ozone treated biochar samples. This reaction pathway has further implication for the stability of the biochar samples, as also shown with the elemental analysis, in that the bulk of the biochar material remains relatively unchanged, meaning that the half-life of the treated biochars is likely still comparable to that of the untreated biochars as predicted with O:C ratios. (Spokas, 2010)

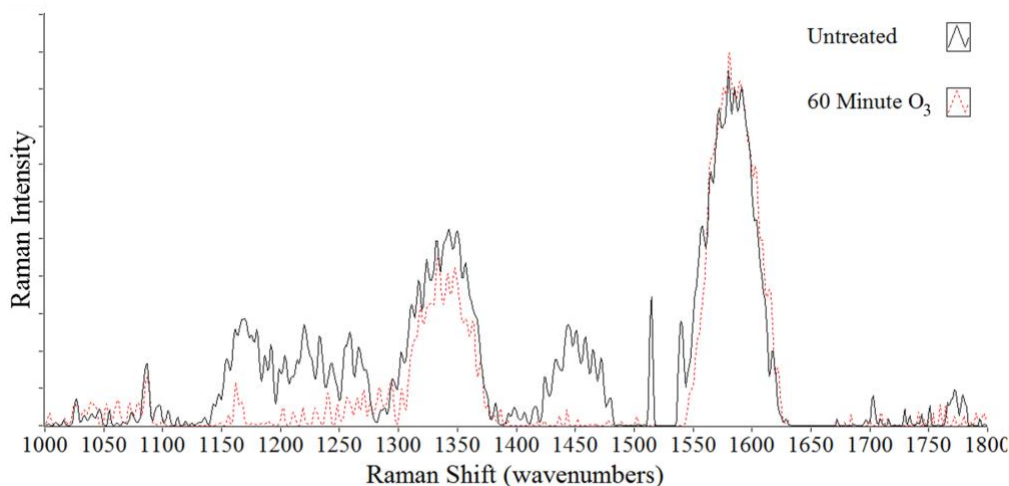


Fig.11. Raman spectra of untreated biochar and biochar treated with 60 minutes of ozone.

4. Conclusions

In conclusion, it has been shown that through the use of ozone treatment on biochar, CEC is greatly increased, the effectiveness of the removal of Cu (II), Ni (II), Cd (II), Pb (II), Zn (II), and Mg (II) from solution is increased, pH is decreased, and the overall bulk composition of the biochar is retained. Furthermore, the FTIR and Raman Spectroscopy measurements indicated that the olefinic groups of the biochar are decreased by ozone treatment, while the overall aromatic carbon structure is left unchanged. Therefore, application of ozone for biochar surface oxygenation has great potential in increasing the value of biochar, especially for widespread use in water and soil remediation for the removal of deleterious contaminants. It is important to note that since ozone can be generated in great quantities in an inexpensive manner from air; this biochar ozonization technology has the potential to cost-effectively convert large quantities of conventional biochars into advanced products with higher CEC values and higher capacity for both organic and inorganic contaminant removal.

CHAPTER V

CONCLUSIONS AND RESULTS

1. Conclusions

The primary goals of this dissertation were to provide a direct comparison of several types of biochar created by both HTC and pyrolysis at varying temperatures and from varying feedstocks, as well as studying the effects of partial oxygenation procedures on aforementioned biochar samples. These goals were accomplished through the use of a wide array of assays. The most important of these assays was arguably the characterization of biochar samples for CEC. CEC, as mentioned previously, is the capacity for the biochar material to retain exchangeable cations, and is an extremely important measure in evaluating the usage of biochar in a widespread manner, especially for agricultural use. It should also be noted that one of the driving factors for large-scale production of biochar is its inherent economic value, and increasing CEC invariably also increases attraction for the use of biochar as both a soil amendment and as a water filtration medium, similar to that of activated carbon, only much more inexpensive. Other assays used in the characterization and evaluation of biochars produced were FTIR-ATR, Raman spectroscopy, water retention capacity, methylene blue adsorption, metal adsorption, gas analysis, pH analysis, and elemental analysis. These particular methods of characterization were extremely useful in determining the physiochemical properties of the biochar samples, which allow for further insight for the optimization of the production and use of biochar.

The first general hypothesis, as put forth in chapter 1 of this dissertation dealt with the direct comparison of HTC and pyrolytic biochars. It was shown that HTC biochars do tend to have higher CEC values than pyrolytic biochars, as well a higher overall biomass to biochar conversion percentage. However, it was also noted that the high O:C ratio of the HTC biochar put forth doubt as to whether or not it would be a suitable material for the long term storage of solid carbon, as it is expected that the half-life in soil would be relatively short. It was also noted that due to a difference in reaction mechanisms, HTC biochars tend to retain much more oxygen functionality when compared to the pyrolytic biochars. This difference also meant that the end product of the HTC process was acidic, whereas pyrolytic biochars were basic. It should also be understood that HTC biochars contain bio-oils in significant amounts, which may cause issues with implementation in soil due to toxicity to crops. When analyzing the different feedstocks of pinewood, bamboo, and peanut shells, it was noted that the conversion method was the most important process in determining overall characteristics of the biochar samples. When comparing solely the pyrolytic biochar samples the yields of biochar lessen with increased temperature, as does the O:C ratio, which is was expected due to the increasing loss of oxygen functionality. The CEC also decreases dramatically with increased treatment temperature. This is an important finding when considering the application of biochar, in that with lower O:C ratios, biochars tend to have much longer half-lives in soil, making them more ideal candidates for long-term carbon sequestration. However, it should also be noted that with lower O:C ratios, biochar has greatly decreased CEC, making such samples not as useful as soil amendments for agricultural use. These findings show that there may not be a truly “ideal” method for the generation of biochar, rather it is a system of trade-offs which should be considered in the specific application of the biochar samples.

After establishing that the several of the attributes of biochar are inherently linked (stability, O:C ratio, and CEC), the research of this dissertation began to focus on discovering a method by which the positive characteristics of biochar could be retained, while avoiding the negative properties yielding from various production methods. To put simply, the primary goal was to synthesize a biochar which had a long half-life, a high O:C ratio on the surface of the biochar, thus maintaining stability, and a high CEC. As stated before however, the biochars which had the highest stability also had the lowest CEC, and this is inherent primarily due to the treatment temperature used. Therefore, it was thought that a highly stable biochar should be made as a first step, to which oxygen functionality could be added back onto the surface in an inexpensive manner which also maintained the core stability of the biochar. As mentioned in the introduction, many industrial processes dealing with activated carbon use oxidation treatments such as KOH, H₂SO₄. These methods have the potential to leave behind unwanted by-products, and require careful safety protocols while in use. In order to avoid this, H₂O₂ was utilized as an oxidant. Having a fairly short half-life, it was known that H₂O₂ would make an ideal candidate for partial oxygenation of biochar, as it breaks down shortly after being synthesized, leaving only water behind. Various concentrations ranging from 1% to 30% w/w of H₂O₂ were utilized to treat biochar samples. It was found that indeed, the treated samples exhibited characteristics of biochars which have high O:C ratios, and yet based on the evidence provided by EA, the majority of the biochar was unchanged, meaning that long term stability had not been compromised through treatment. Furthermore, it was found that CEC was greatly improved with H₂O₂ treatment, providing evidence for added economic value for the biochar samples. Interestingly though, the biochars treated with higher concentrations of H₂O₂ showed a downward trend for the absorbance of methylene blue, which is thought to have been caused by

the destruction of some of the surface aromatic rings of the biochar samples, as evidenced by the FTIR-ATR spectra. This gives some insight into the functionality that H_2O_2 interacts with on the biochar, as well as demonstrating information as to the mechanism of adsorption of methylene blue. Methylene blue is a three ringed, aromatic compound with a native positive charge, and therefore it was thought that with increased cation exchange due to greater negative overall charge on biochars, that the methylene blue adsorption would have increased. However, these findings point towards the mechanism of adsorption by π - π stacking to be more important than electrostatic interactions.

Once it had been established that oxidants such as H_2O_2 could be used to improve biochar CEC, while retaining the core stability of the biochar, it was proposed that O_3 be used in a partial oxygenation procedure. O_3 has a higher oxidation potential than H_2O_2 , (2.07 to 1.78, respectively) and that therefore, it would be an even more effective oxidant (Parsons, 2004). Additionally, O_3 has the added property of being a gas at room temperature, and having an even shorter half-life than H_2O_2 , meaning that after treatment, one simply turns off the ozone generator and waits a shorty period of time for any possible unwanted by-products to dissipate. Another advantage of the use of O_3 is that it can be simply and inexpensively generated on-site in large quantities through the use corona discharge. This is an important consideration for the economics of post-treatment of biochar, as it could then be done in remote sites which may not otherwise have access to other types of partial oxygenation treatments. The results of the use of O_3 were extremely promising, producing a doubling of CEC for the 30 and 60 minute treatment times. Furthermore, as was the case with H_2O_2 , it was found that most of the oxygenation had been done only on the surface of the samples. EA revealed that there was less than a 0.05 difference in the O:C ratios of the untreated biochar and the biochar sample that was treated with

90 minutes of O_3 , which means that the overall bulk of the biochar was not augmented, and therefore overall stability maintained. One of the drawbacks found with the use of O_3 for partial oxygenation, was that while reacting with the biochar, a significant amount of heat was generated. This poses a potential issue with scaling up this process in that a large amount of biochar being treated with O_3 in a high oxygen environment has the likelihood of combusting, which obviously, is dangerous to both equipment and personnel. However, this can be mitigated through reactor design and the use of wet ozonization. A second drawback to O_3 treatment was that the process does release some CO_2 , therefore it is necessary for further research to minimize this undesirable side effect, potentially by elucidating the mechanism by which the biochar is reacting with ozone. Interestingly, it was found that methylene blue adsorption was greatly increased with the use of O_3 treatments, which is in direct contrast to the treatments performed with H_2O_2 . It is thought that O_3 attacks primarily the olefinic groups on the biochar surface, while hardly affecting the aromatic portions. This was elucidated through the use of Raman spectroscopy, which shows a marked decline in the olefinic functionality, while the aromatic portion remains mostly the same when comparing untreated and treated biochars. This conclusion could not have been made through solely the use of FTIR-ATR, and reveals information about the mechanism by which O_3 reacts with biochar. The FTIR-ATR spectra were also performed multiple times as shown below to ensure that the results were reproducible. A peak at 875 cm^{-1} resembles residual carbonate, which is well known to be a scavenger for radical ions, thus explaining the disappearance of the aforementioned peak during ozone treatment (Reig et al., 2002).

Overall, this research concludes that it is possible through the use of surface oxygenation procedures, it is possible to generate biochar samples that both maintain long-term stability as

exhibited by their O:C ratios, while greatly increasing their positive characteristics such as CEC and methylene blue removal. This confirms the original hypothesis found in chapter one and provides an excellent framework for future research projects. It is clear though, that while much progress has been made, many more advances will be needed before the widespread use of such partial oxygenation processes are seen.

2. Future Work

There are many logical directions for future research projects that could be based on the findings in this dissertation. While the information contained above is useful, it of course is not exhaustive. This being the case, this section lists specific ideas for the broadening of several of the chapters, with specific attention to the scaling up of processes, economic feasibility, as well as the elucidation of the mechanisms by which the partial oxygenation processes occur.

As mentioned in the introduction section, the use of biochar as a substitute for activated carbon in the role of metal removal from effluent waste streams has garnered much attention recently (Anderson et al., 2013). Future work in this section will involve furthering the field of study by using biochars treated with H_2O_2 and ozone and comparing the impact of the biochars on metal adsorption in large water bodies. In a recent publication that cited the work shown in chapter 3, it was revealed that biochars treated with H_2O_2 showed a marked improvement in the removal of copper from solution (Zuo et al., 2016). However, it should be noted that this paper only researched the removal of copper from solution, and it would be beneficial and novel to produce a broader paper involving a wider array of metals including cadmium, lead, magnesium, and calcium for example. Another variable that could be tested in this project is contact time with the metal solutions and biochar, as well as varying the metal containing solutions by pH.

Furthermore, while batch studies are commonly employed in such experiments, it would be useful to also do column studies, wherein a larger amount of biochar (~10 grams) is placed into a glass column, and aqueous metal solutions are then poured over and allowed to flow through the column. A column experiment is more similar to real world applications and can also be helpful in determining breakthrough points of metal contaminants in water systems. Another attribute that can be tested is the wettability of the biochar both before and after oxygenation treatment, which can have substantial applicability not only in wastewater streams, but also in terrestrial systems. A second paper that can be produced from this research is the comparison of untreated biochars and biochars treated with ozone on metal removal in aqueous systems. Much like the H_2O_2 project listed above, this future paper will evaluate the effectiveness of ozone treatment of the removal of various metal contaminants over a range of pH values as well as contact time. These two projects will help develop understanding the effects of the two different oxygenation techniques and by elucidating the structural changes from each treatment on the biochar, more knowledge will be gained on exactly what types of functionality are best to be introduced onto the biochar surface for metal removal. It will then be possible to make recommendations for larger scale experiments in order to remove metal contaminants from actual wastewater effluent streams.

Another relevant project that could be explored is the characterization of the material which is solubilized by the process of ozone treatment. It has been recently noted that there is a difference between the color of filtrates resulting from the rinsing of biochars before and after different durations of ozone treatment. In order to characterize this material, samples of biochar will be treated with ozone and have water flowed over them. It is thought that by taking these filtrates and analyzing them through several different methods, the mechanism by which ozone

reacts with the biochar surface could be better elucidated. Specifically, the filtrate will be collected and freeze dried and will then be analyzed by Raman, FT-IR, Mass spectrometry, EEMS, elemental analysis, and NMR (filtrate resuspended in D₂O), and dissolved organic carbon measurement. If a high enough concentration of the filtrate can be dissolved in D₂O for NMR analysis, it would be useful not only to run the standard ¹³C and ¹H NMR analyses, but also several 2D techniques such HSQC, HMBC, and COSY analyses. It is expected that much of the filtrate will be mostly carbon so both APT and DEPT analyses would be expected to yield useful results. Elemental analysis will be performed in order to verify the composition of the samples. Each of these analyses will be utilized to further improve the exact concentrations of ozone as well as the duration of ozone treatment to ideally react with biochars.

A secondary analysis of the filtrate material would be to measure its effects on algae growth, and verify whether it is toxic or not. If toxic, an LC-50 could be calculated and reported in order to ensure the safety of the ozone treatment as far as runoff after introduction to soils are concerned. This is an especially important factor to consider when planning on the use of ozone treatment of biochar at a large scale.

As shown in chapter I of this dissertation, both feedstock and pyrolysis temperature, as well as the carbonization process (pyrolysis vs. HTC) play a large role in the characteristics of the resultant biochars. This being the case, it would be interesting to produce a variegated array of biochars produced from a number of different biomasses, (i.e. switchgrass, pinewood, cornstover, etc) produced by either pyrolysis or hydrothermal conversion over a range of temperatures. Another possibility for this is to use different fractional mixtures of both pure lignin and cellulose in order to yield data based on the primary components of most biomasses used in making biochar in order to gain the broadest picture possible. After production of each

type of biochar over a variety of settings, the biochar would then be treated with varying durations of ozone. Both before and after ozone treatment, each type of biochar would then be tested for CEC, methylene blue adsorption, pH, and water retention capacity. Each biochar sample would also be analyzed with FT-IR, Raman, and elemental analysis in order to more fully characterize the structure of each biochar. As seen in chapter I, biochars produced at lower temperatures via pyrolysis had higher CEC values, as well as lower pH values when compared to biochars produced at higher pyrolysis temperatures. Structurally, biochars produced by pyrolysis at lower temperatures when compared to those produced at higher temperatures retain more oxygen functionality, as revealed by both EA and FT-IR. It is important to note here that the biochars produced at higher pyrolysis contain a higher percentage of fixed carbon, meaning that their lifetimes in soil serving as a carbon sequestration agent are much longer than that of the biochars with lower fixed carbon content. As mentioned throughout this dissertation, it is important to strike a balance between both high CEC and long term stability in soil. With the treatment of ozone of many different types of biochar, it will be revealed to what extent oxygenation can occur, and which biochars are more amenable to zone treatment in terms of increasing CEC while maintaining bulk stability. By testing a large variety of biochars this way, it may then be possible to begin optimizing the partial oxygenation process and gain greater insight as to what to expect if the partial oxygenation process is scaled up. For instance, preliminary results from chapter IV of this paper lead to the conclusion that it is mainly the methylene portion of the biochar functionality that is readily reacted with by ozone treatment, while the disordered and ordered graphite portions of the biochar surface are relatively unchanged. Additionally, it must be understood that thermodynamically, graphitic structures are relatively unreactive, which leads to the long term stability of biochar. It is well known that

biochars begin to be more graphitic in nature as the pyrolysis temperature is increased, therefore limiting the amount of functional sites which can be readily attacked by ozone treatment. Therefore, one of the primary goals of this project would be to identify both the biomass and highest treatment temperature which yield an optimal amount of both graphitic structure and retained methylene groups which can be reacted with ozone in order to increase favorable surface functionality while maintaining long term stability. In short, it would lead to the tailoring of the ozonization process depending on the inherent feedstock and temperature from which the biochar is created. This is an important venue to explore, especially as biochar use becomes more widespread for two main reasons: There is no set type of ideal large scale pyrolysis reactor yet established; and feedstocks for biomass can come from a very wide array of sources.

Elemental analysis was also performed again in triplicate on the samples shown in the fourth chapter of the dissertation. Additionally, several additional studies were completed using ATR-FTIR to verify the results within the third paper. Whilst slightly different from the previous samples of pinewood derived biochar, the spectra were reproducible as shown below and in the fourth chapter. The highlighted peaks at 1590 cm^{-1} , 1440 cm^{-1} , 1200 cm^{-1} , and 875 cm^{-1} represent aromatic elastic and inelastic C=C, aromatic CO stretching, and carbonate, respectively (Özçimen et al., 2010).

The FTIR-ATR spectra of the same ozonized and control biochar samples were re-measured using a second instrument (Bruker Alpha FT-IR spectrophotometer) to ensure reproducibility. The FTIR-ATR spectra re-measured by the author and independently by Gyan Kharel were presented in figures 12 and 13, respectively. It was noticed that the re-measured FTIR-ATR spectra (figures 12 and 13) varied somewhat from that of the early measurement

(figure 8) which was measured with a Shimadzu IRPrestige-21 FT-IR spectrophotometer. The peak at 875 cm^{-1} shown in figure 8 in the untreated sample is consistently observed also in the re-measured FTIR-ATR spectra (figures 12 and 13). However, the peak at 1440 cm^{-1} seen in figure 8 is not observed as strongly in re-measured FTIR-ATR spectra. There is a reduction in the peak at 1440 cm^{-1} that can be seen in all 3 figures, however it is not as easily defined in figures 12 and 13. This difference for this peak (1440 cm^{-1}) between the early result (figure 8) and the recent re-measurement (figures 12 and 13) is most likely due to a difference in the type of ATR utilized, as well as two somewhat different instruments: 1) ZnSe trough ATR used in a Shimadzu IRPrestige-21 FT-IR spectrophotometer for figure 8; and 2) Diamond plate ATR for figures 12 and 13 used in a Bruker Alpha FT-IR spectrophotometer.

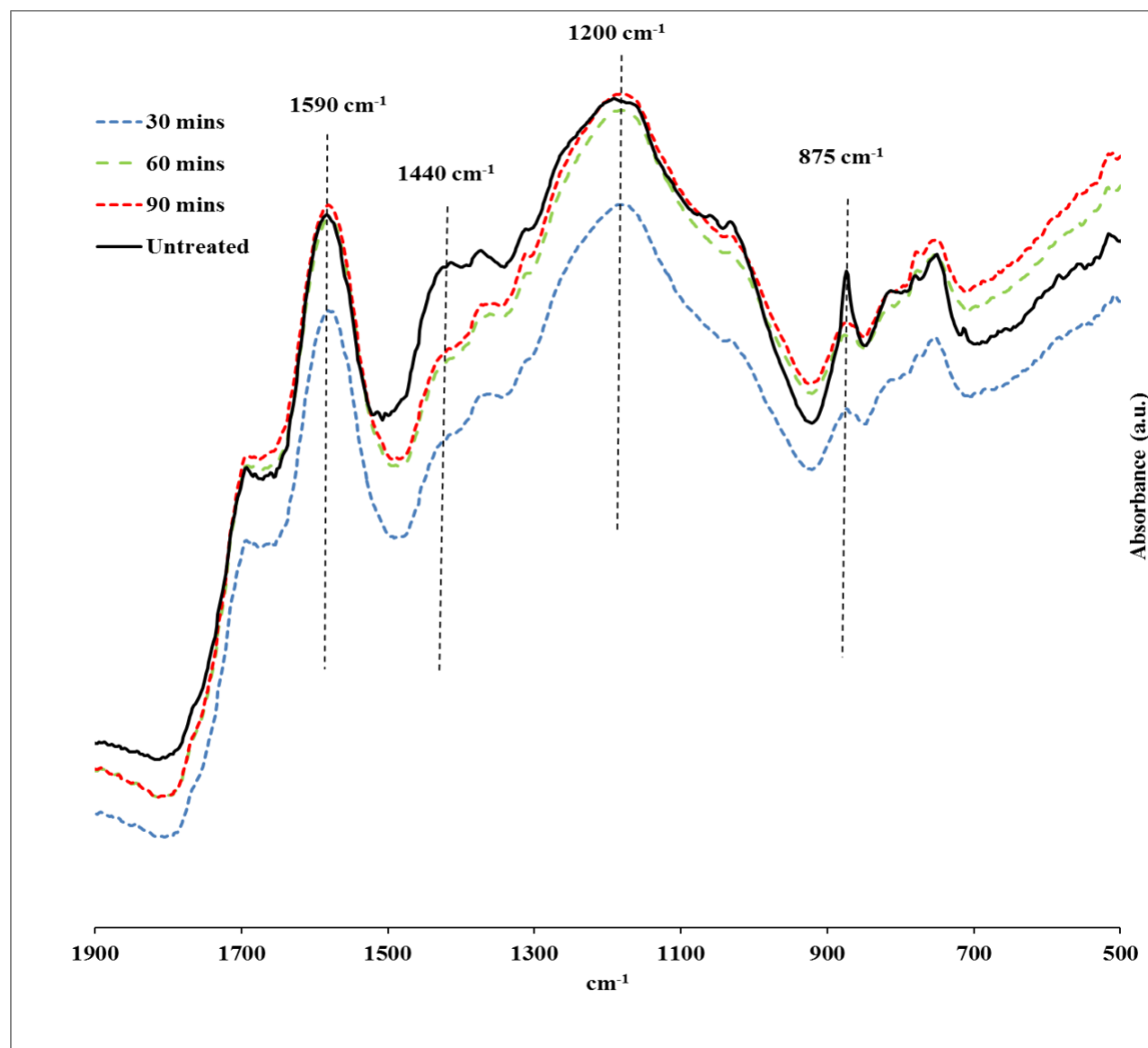


Fig. 12. Trial 4 of FTIR-ATR spectra of untreated and ozone treated biochars measured with the Bruker Alpha instrument by Gyan Kharel.

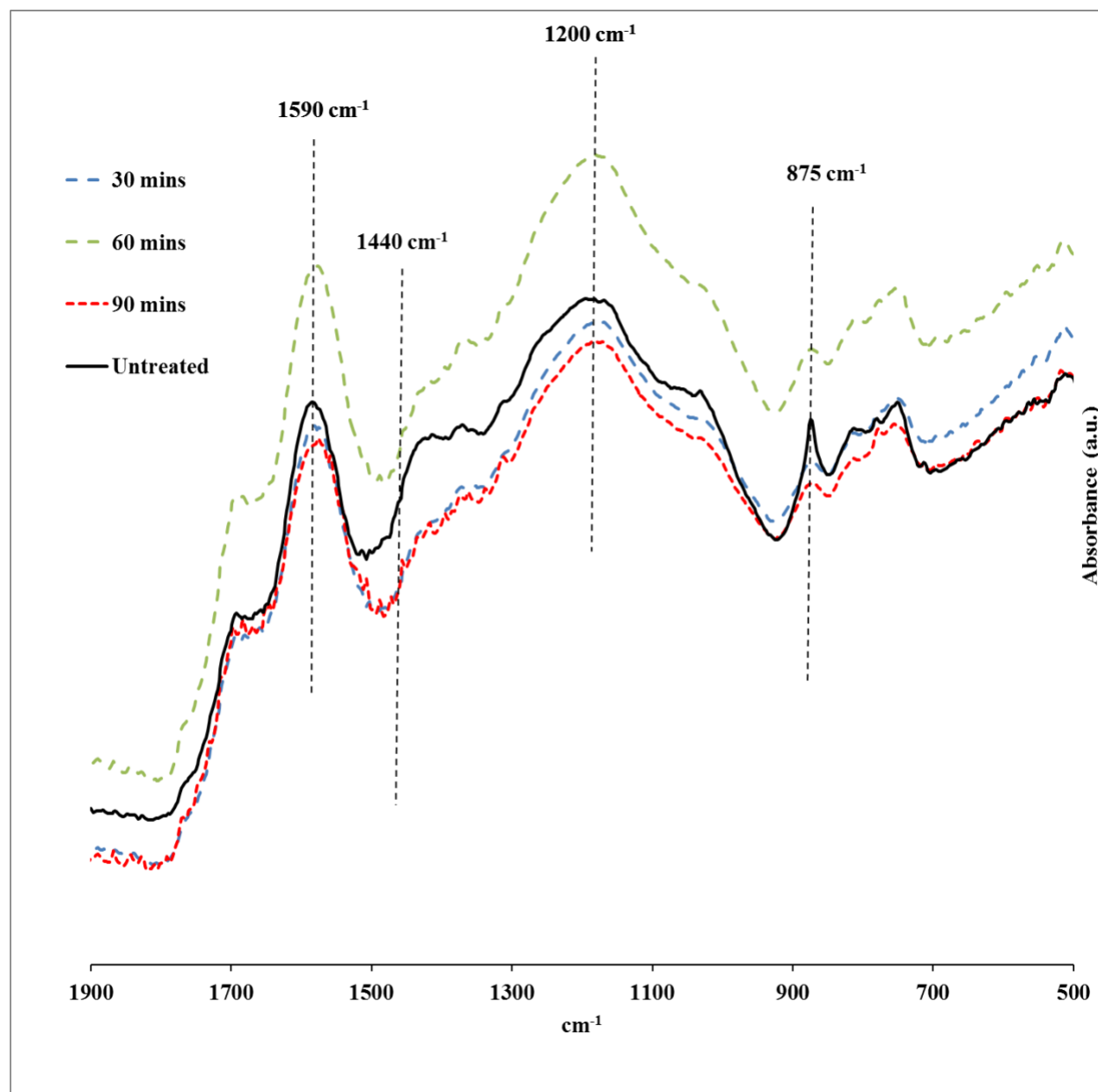


Fig. 13. Trial 5 of FTIR-ATR spectra of untreated and ozone treated biochars measured with the Bruker Alpha instrument by the author of this dissertation.

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APPENDIX A

ABBREVIATIONS AND ACRONYMS

AA	atomic absorption
AOAC	association of analytical communities
APT	attached proton test
C	carbon
CEC	cation exchange capacity
COSY	homonuclear correlation spectroscopy
CSiTE	carbon sequestration in terrestrial ecosystems site
DBR	distributed bragg reflector
DEPT	distortionless enhancement polarization transfer
EEMS	excitation-emission matrix spectroscopy
FTIR-ATR	Fourier transform infrared- attenuated total reflectance
GTC	giga-tons-carbon
H	hydrogen
H ₂ O ₂	hydrogen peroxide
HMBC	heteronuclear multiple bond correlation
HSQC	heteronuclear single quantum coherence
HTC	hydrothermal conversion
HTT	highest treatment temperature
K ⁺	potassium ion
Meth. Blue	methylene blue
MW-SSE	moving-window sequentially shifted excitation
N	nitrogen
NH ₄ ⁺	ammonium ion
NMR	nuclear magnetic resonance
O:C	oxygen to carbon ratio
O ₃	Ozone
RCF	relative centrifugal force

UGA	universal gas analyzer
UV	ultraviolet
Vis	visible
w/w	weight-to-weight

VITA

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EDUCATION

Aug. 2011 — present **Old Dominion University (ODU), Norfolk VA, USA**
 PhD Candidate- Chemistry
 Expected date of graduation: Fall 2018
 Concentration: Environmental/Material Chemistry

Aug. 2009 — Jul. 2011 **University of North Carolina -Charlotte, Charlotte, NC**
 Master of Science in chemistry program

Aug. 2005 — May. 2009 **Hampden-Sydney College, Hampden Sydney, Va**
 Bachelor of Sciences Degree, 2009
 Major: Chemistry

RESEARCH EXPERIENCE

Old Dominion University, Norfolk, Va:

August 2011 – present **Department of Chemistry and Biochemistry. PhD Candidate**

- Explored the relationship between biomass input and conversion process of biomass for end-product validation of biochar characteristics
- Investigated the relationship between the O:C ratio of carbon rich samples and the ability for the samples to facilitate cation exchange, methylene blue adsorption, and water retention for potential use as a soil amendment
- Utilized FT-IR, elemental analysis, and Raman spectroscopy in order to analyze carbon rich samples with regards to surface functionality.
- Employed flame AA and designed a series of experiments to evaluate various materials capacity for the removal of unwanted metal contaminants from aqueous systems such as iron, copper, lead, cadmium, and selenium, and developed processes to enhance the various materials' efficacies.
- Investigated the relationship between highest treatment temperature of solid carbon residues and overall long-term stability of solid carbon residues as a function of oxygen content.
- Assisted in the preparation of several NSF grants concerning the implementation of research into processes to create high-tech solid carbon residues for sustainable carbon sequestration
- Experienced with: HPLC, Raman spectroscopy, 2-D NMR analysis, Differential scanning calorimetry, Thermogravimetric analysis, Graphite furnace atomic absorption, UV-Vis spectroscopy, Fluorescence spectroscopy, Fourier transform infrared spectroscopy, GC-MS, and GC-FID

PUBLICATIONS

- **Huff, Matthew D.**, and James W. Lee. "Biochar-surface oxygenation with hydrogen peroxide." *Journal of Environmental Management* 165 (2016): 17-21.
- **Huff, Matthew D.**, Sandeep Kumar, and James W. Lee. "Comparative analysis of pinewood, peanut shell, and bamboo biomass derived biochars produced via hydrothermal conversion and pyrolysis." *Journal of environmental management* 146 (2014): 303-308
- **Huff, Matthew D.**, and James W. Lee. "Biochar-surface oxygenation with hydrogen peroxide." *Journal of Environmental Management* 165 (2016): 17-21.
- Abdel-Fattah, T. M., Mahmoud, M. E., Ahmed, S. B., **Huff, M. D.**, Lee, J. W., & Kumar, S. "Biochar from woody biomass for removing metal contaminants and carbon sequestration." *Journal of Industrial and Engineering Chemistry* (2014).
- Porterfield, W. W., Zrelak, G. M., Moncure, L. A., & **Huff, M. D.** "Continuous conversion of methanol to higher hydrocarbons at ambient pressure." *Journal of Natural Gas Chemistry* 19.5 (2010): 461-462.