



## Research paper

## Enhancing cation exchange capacity of chars through ozonation

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## ABSTRACT

The use of ozone to increase the cation exchange capacity (CEC) of two chars produced from pyrolysis of Douglas fir (*Pseudotsuga menziesii*) and a control bituminous coal activated carbon (AC) is reported. Chars were produced from the wood fraction of Douglas fir (DFWC) and the bark (DFBC) at 500 °C using an auger driven reactor with a nitrogen sweep gas under mild vacuum. Five ozone treatment times, ranging from 5 min to 60 min, were investigated. The initial properties of each char were found to differ significantly from the other samples in terms of surface area, proximate composition, and elemental composition. DFWC did not show significant mass loss or temperature variation during ozone treatment; however, after 1 h of oxidation both DFBC and AC samples resulted in 20% and 30% mass loss, respectively, and reactor temperatures in excess of 60 °C. Analysis of the pore size distribution of each treatment shows that ozone treatment did not significantly affect small micropores after 30 min of treatment for any material, but did reduce the apparent surface area of mesopores. Increases in carboxylic groups were identified with ozone treatment and found to correlate strongly with changes in measured CEC. The formation of lactone was found to correlate positively with reactor temperature during oxidation. These results indicate that the properties of chars, including surface area, pore structure, and chemical composition, as well as reactor conditions strongly affect the ozone oxidation of chars.

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## 1. Introduction

Chars and activated carbon have a long history of use in adsorption processes. The work of Lehmann in the early 2000s on Terra Preta soils from the Amazonian Basin brought renewed focus on the potential use of chars for agronomic purposes [1,2]. Evidence suggests that char-like materials have substantially altered physical and chemical properties in these soils, leading to long lasting carbon storage and improved crop production. Reviews by Glaser et al. [3], and by Blackwell et al. [4] show generally positive effects of char addition to soil, though some negative effects have been reported. The effectiveness of char remediation treatments were found to be sensitive to the rate of addition [5], soil type, and initial feedstock [6]. Despite a range of studies aimed at investigating the effectiveness of chars in soils, assessment of the physicochemical structure of the char used for treatment is often not explored,

leaving numerous possibilities for the disparity in observed effects.

Several physical and chemical properties are known to impact the behavior of char in soils, including surface area, porosity, and the quantity of acid exchange sites on the char in relation to the soil. Higher quantities of acidic exchange sites have been identified in Terra Preta soils as compared to adjacent soils [2]. These sites exist primarily in the form of weakly acidic carbon-oxygen groups that can chemically bind Lewis bases, such as metal or ammonium ions in solution. Based on this principle, oxidized chars and activated carbons have been investigated for the removal of ammonia from gas streams and ammonium from liquid streams [7–12]. Chiang et al. [12] has shown a strong correlation between the quantity of ammonia adsorbed by treated carbons and the concentration of acid groups on the surface.

The development of carbon-oxygen groups on a freshly produced char surface can take months to years to develop under ambient conditions [13]. Research groups have investigated various methods to more rapidly oxidize carbon surfaces; mechanisms studied include strong acids [9], oxygen at elevated temperatures [14], and ozone [7,8,10,12–18]. While acid treatment methods are

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effective, the cost of facilities, materials, and post-treatment of liquid effluents increases material handling costs and complexity. Formation of acid groups through gas phase reactions can limit secondary treatment requirements and can be achieved through the use of either air or ozone. While ozone requires special handling and disposal, reactions can be carried out under ambient conditions, whereas air oxidation requires elevated temperatures to progress at a substantive rate.

In addition to studies with activated carbon, the reaction of moderate temperature wood chars with ozone has also been investigated [10,13]. Analysis of the changes in surface chemistry, and the relation of these changes to the cation exchange capacity (CEC) of these chars was not reported. Here the effects of ozone on the surface characteristics are examined through chemical and spectroscopic analysis to investigate how surface properties, including CEC, develop on chars during ozonation.

## 2. Experiments and methods

### 2.1. Chars

Douglas fir (*Pseudotsuga menziesii*) wood (DFW) and bark (DFB), harvested from the Cascades region of Washington State has been provided by Herman Brothers Logging & Construction (Port Angeles, WA) from standard mill operations. The received chips were ground to below a 2 mm sieve size by hammer milling (model number 400 HD, serial number 2404, Bliss Industries, Inc). Ground samples were stored in polypropylene bags at 4 °C in a dark environment. Composition of each sample is reported in Table 1 and was measured in duplicate following standard methods provided by the National Renewable Energy Lab [19,20].

Prior to pyrolysis samples were dried overnight at 105 °C. Chars from the DFW and DFB samples (DFWC and DFBC, respectively) were produced in a 1 kg h<sup>-1</sup> auger-driven reactor at Washington State University following the methodology described elsewhere [21]. Briefly, the reactor's external wall temperature was maintained at 500 °C with a particle residence time of approximately 1 min. Nitrogen was used as a carrier gas at 10 L min<sup>-1</sup> to ensure an oxygen-free atmosphere. Char temperature at the reactor exit was determined to be between 270 and 370 °C. A vacuum pump maintained a slight negative pressure of 20 Pa (2 mm H<sub>2</sub>O) inside the reactor to ensure forward gas flow. Char samples were collected by gravity from the auger line. Visual inspection of the final product did not indicate the presence of residual unconverted biomass in the collected samples. Pyrolysis of the wood fraction resulted in a char yield of 20 mass %, while the char yield of the bark fraction was 24 mass % char on an oven dry basis. The resulting char products were stored in sealed polypropylene bags under ambient conditions in a dark environment until ozone oxidation treatments.

A commercial activated carbon (AC) produced from bituminous coal was purchased from Sigma Aldrich (Sigma Aldrich 242268 Lot 33896CJ, manufactured July 2008) and used without modification in the ozone treatment experiments.

### 2.2. Ozonation

Each feedstock was oxidized under ozone using approximately 3.0 g of sample per run in a 316L stainless steel (SS) packed-bed reactor with an internal diameter of 7.29 cm. Samples were supported on a 150 μm 304 SS screen. All connections and peripherals were constructed of 304 S S, 316 SS, or polytetrafluoroethylene material. Ozone was generated by a corona-discharge type system (Lab-11 ozone generator, Pacific Ozone Technology, Inc., Benecia, CA) using purified oxygen gas (minimum purity 99.5%). Five oxidation times were used for each material ranging from 5 min to 60 min (numerical suffix of 0–60 denotes ozone oxidation time for each sample), with all treatments run in triplicate. All tests were carried out at an average ozone concentration of 70 mg L<sup>-1</sup> in a 2.0 L min<sup>-1</sup> oxygen/ozone stream (all gas volumes reported at standard conditions of 298 K and 101.3 KPa). The temperature of the char within the packed bed was measured by a type-K thermocouple (Omega Engineering, Inc., Stamford, CT). The concentration of ozone was measured by an iodine wet chemistry method outlined by Rakness et al. [22].

### 2.3. Bulk properties

Ash content of the initial samples was determined in triplicate using a high-temperature furnace to determine the ash fraction following ASTM method D1102-84 [23]. 1.1 g ± 0.1 g of air-dry material was heated in air at 575 °C for 12 h, and the ash fraction determined on an air-dry basis. Volatile matter and fixed carbon were determined in triplicate for each initial and ozone treated sample using thermogravimetric analysis (Mettler Toledo TGA/SDTA851e) based on methods described in ASTM method E1131-08 [24]. Alumina crucibles were loaded with 6 mg–7 mg of sample and heated under nitrogen (minimum purity 99%) flowing at 50 ml min<sup>-1</sup>. The heating program used is as follows: from 25 °C to 105 °C at 10 K min<sup>-1</sup> with a 15 min hold, and from 105 °C to 650 °C at 30 K min<sup>-1</sup> with a 10 min hold. Mass loss at 105 °C was attributed to moisture and highly volatile matter while mass lost between 105 °C and 650 °C was attributed to volatile matter. The solid fraction remaining is attributed to fixed carbon and ash. The moisture content determined by TGA was used to correct the ash fraction to an oven-dry basis.

Elemental analysis for carbon, hydrogen and nitrogen was determined on an oven-dry basis and conducted by the University of Washington Oceanography Department using a Leeman Labs Model CEC440 elemental analyzer. A sample size of 2.5–4.0 mg was used. The equipment was calibrated using acetanilide and caffeine standards. Calibration was checked by a caffeine deviation of less than 1%. Oxygen was determined by difference.

Mineral analysis was conducted using an ICP-MS (Agilent 7500cx series) equipped with a double-bypass quartz spray chamber with a quartz nebulizer. To prepare the analysis solutions, 0.1 g–0.2 g of each char and AC were pre-digested using 3.0 ml of concentrated NHO<sub>3</sub> and 2.0 ml of 30 mass % H<sub>2</sub>O<sub>2</sub> in a microwave digester (SP-D, CEM Corporation, Matthews, NC). Digestion was carried at out 300 °C and 1.72 MPa for 5 min. A 5 min ramp was used to reach digestion conditions. Digest samples were diluted to

**Table 1**  
Composition of initial biomass, all results reported as mass fraction (%).

Sample	Hemi-cellulose	Cellulose	Lignin	Extractives	Insoluble ash	Total
DFB	8.8 (0.2)	18.2 (0.3)	43.4 (1.3)	19.5 (0.6)	1.65 (0.35)	89.3 (0.8)
DFW	17.0 (0.1)	43.2 (0.2)	29.9 (1.5)	5.2 (ND)	<0.1 (<0.1)	95.2 (1.8)

ND: Results from single trial, no deviation could be determined.

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