

Biochar Surface Oxygenation by Ozonization for Super High Cation Exchange Capacity

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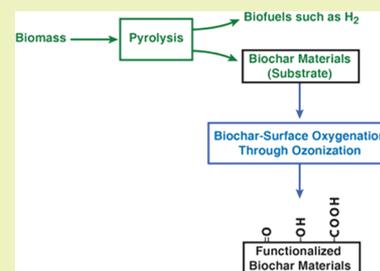
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Supporting Information

ABSTRACT: Biochar cation exchange capacity (CEC) is a key property central to better retention of soil nutrients and reduction of fertilizer runoff. This paper reports a breakthrough process to improve biochar CEC value by a factor of nearly 10 through biochar surface oxygenation by ozonization. The CEC value of the untreated biochar was measured to be anywhere between 14 and 17 cmol/kg. A 90 min dry ozonization treatment resulted in an increased biochar CEC value of 109–152 cmol/kg. Simultaneously, the biochar ozonization process resulted in a reduction of biochar pH from 9.82 to as low as 3.07, indicating the formation of oxygen-functional groups including carboxylic acids on biochar surfaces. Using the technique of X-ray photoelectron spectroscopy (XPS), the formation of oxygen-functional groups including carboxylic acids on biochar surfaces have been observed at a nanometer molecular scale following the ozonization treatment. The molar O/C ratio (0.31:1) on ozonized biochar surface as analyzed by XPS was indeed significantly higher than that (0.16:1) of the control biochar surface. The molar O/C ratio from the elemental analysis data also showed an increase from the nonozonized sample (0.077:1) to the dry-ozonized sample (0.193:1). Fourier-transform infrared (FTIR) spectroscopy analysis also showed an increase in the content of oxygen-functional groups in the form of carbonyl groups on biochar surfaces upon ozonization, which can also produce certain amount of oxygenated biochar molecular fragments that may be solubilized by liquid water, potentially leading to greater effects upon application of biochar in soil.

KEYWORDS: Biochar surface oxygenation, Cation exchange capacity, Biochar ozonization, X-ray photoelectron spectroscopy, Oxygen functional groups on biochar surface



INTRODUCTION

Biochar, a carbon-rich soil amendment, has been used for several centuries to improve soil fertility and increase yield. While recent interest in biochar has produced an abundance of scientific knowledge, variability in the physiochemical properties of biochar and an inability to predict biochar-soil interactions and agronomic outcomes have stifled the implementation of biochar-related practices. While some studies show improvements in crop production and soil fertility following biochar amendment, meta-analyses also demonstrate no improvements or declines in crop production in a large fraction of studies.^{1–3}

The enhanced fertility of soils historically amended with charcoal, such as Amazonian Terra Preta soils, can be partially attributed to improved cation exchange capacity (CEC).^{4,5} CEC is a key indicator of soil fertility, buffering capacity, and water holding capacity.^{6–8} However, many contemporary biochars have a low CEC (mostly below a typical soil CEC value of 15 cmol/kg) and weathering studies have demonstrated that the natural surface oxygenation of biochar develops at decadal time scales.^{9–11} Thus, the variability of crop

response to biochar-amended soils may be attributed to their low CEC.^{12,13,7,14–16} Therefore, biochars with greater CECs are critically needed to achieve the mission of biochar as a soil amendment and carbon sequestration agent.^{17–20}

While a high O/C ratio may be desirable for high CEC,²¹ it must also be understood that the higher the O/C ratio, the shorter the overall half-life of biochar when placed in soils. Biochars with O/C ratios <0.2 have half-lives more than 1000 years in natural soil environments.²² The expected half-lives drop precipitously to <100 years for an O/C ratio of ≥0.6. An ideally designed biochar for use as both a soil amendment and carbon sequestering agent would need to enhance the O/C ratio only on the surface of biochar,²³ giving a higher CEC, while still maintaining the poly aromaticity (preferably lower O/C ratio) of the biochar core to ensure long-term stability.

This article reports a technological solution that dramatically increases the CEC of biochars through surface oxygenation.

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The underlying concept is that an innovative application of postproduction biochar ozonization (Figure 1) can cost-

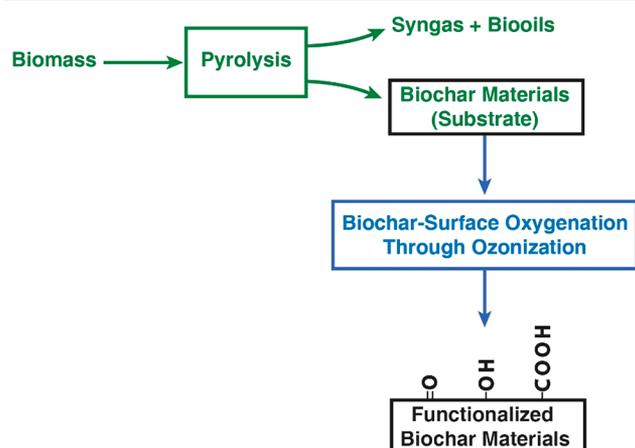
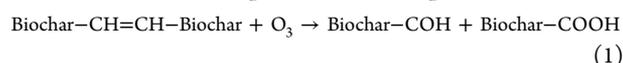


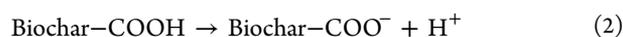
Figure 1. Schematic for postproduction biochar ozonization to create oxygen containing functional groups on biochar surfaces.

effectively create oxygen-containing functional groups on biochar surfaces that will substantially increase its CEC and improve its performance in agronomic and remediation applications.

According to our preliminary understanding,^{23,24} the most significant reactions of O_3 with organic matter are likely based on the cleavage of the carbon double bond, which acts as a nucleophile having excess electrons. The injected O_3 stream may lead to the formation of carbonyl and carboxyl groups on biochar surfaces by reacting with carbon-carbon ($C=C$) double bonds at ambient pressure and temperature.



In this case, the ozonized biochar will become more hydrophilic since both carbonyl and carboxyl groups can attract water molecules. Because the carboxyl groups readily deprotonate in water and result in more negative charge on biochar surfaces, it will also increase the CEC.



In a previous study,²³ we tested this biochar ozonization process and observed an increase in the CEC value of the biochar by a factor of nearly 2. In the present study, using a biochar material with high BET surface area, the use of ozonization resulted in an increase in biochar CEC to over 100 cmol/kg , which may represent a significant breakthrough in biochar science and technology.

MATERIALS AND METHODS

Characterization of Biochar. The Rogue Biochar used during the experiment was obtained from Oregon Biochar Solutions. According to the company, the biochar was made from softwood tree materials such as Douglas fir, sugar pine, etc. The biochar was characterized by the International Biochar Initiative (IBI, Lab ID number 7020309-01). The characteristics of the Rogue biochar are represented in Table S1 of the Supporting Information.

Dry Ozone Treatment. The Rogue biochar obtained from Oregon Biochar Solutions was oven-dried overnight at 105°C in an electric oven. The biochar was then ground, sieved using a $106\ \mu\text{m}$ sieve, washed with ultrapure water (100 mL per gram), and placed back in the oven at 105°C overnight for drying. This biochar is referred to as RBC UN in the paper. A 1.5 g portion of the oven-dried

biochar was weighed and placed in an ozone treatment vessel. The ozone generator (Welsbach T-series) was set to optimum condition for the generation of ozone as described next. Briefly, the oxygen pressure was set to 8 psi, and the flow of oxygen/ozone was set to 3 L/min. The ozone gas stream was passed into the sample containing reactor vessel for a duration of 90 min. During the treatment, the sample reactor vessel was shaken in regular intervals of 15 min in order to treat every particle of biochar with ozone. After 90 min, the biochar was washed thoroughly in two steps with ultrapure water. The first rinse of 25.0 mL and the second rinse of 300 mL were both collected in vessels for subsequent dissolved organic carbon (DOC) determination. The washed biochar was then placed in the oven at 105°C for drying. This ozonized biochar is called as RBC 90D in the paper. Proportional amounts of ultrapure water were also used to rinse 3 g of RBC UN biochar, and filtrates were collected for subsequent DOC determination.

pH Determination. The biochar pH was recorded with a Beckman Coulter Phi 570 pH meter connected to a Thermo Scientific Orion pH probe. To determine the biochar pH, three replicates of 1.0 g each of RBC UN and RBC 90D biochar were taken and placed into 50 mL centrifuge tubes with 10 mL of ultrapure water added to each tube. For the RBC 90D biochar, pH was determined both before and after the rinsing procedure described above, in order to determine the impact of the DOC component. The tubes with the mixture were then placed on a shaker Innova 2300 platform shaker (New Brunswick Scientific, Eppendorf AG, Germany) and the shaker was set at 120 rpm for 1 h. After shaking, the pH of the slurry of each sample was recorded.

CEC Measurement Using the AOAC Method (at the ODU Laboratory). To determine the biochar CEC, a similar approach with a modified protocol from AOAC method 973.09 as reported by Rippey et al. (2007) was used.²⁵ Briefly, six replicates of 0.5 g each of RBC UN and RBC 90D biochars were taken and each of the 0.5 g samples was placed into a 125 mL Erlenmeyer flask with 50 mL of 0.5 M hydrochloric acid (HCl) added to each flask. The flasks with the mixture were then placed on the shaker set at 120 rpm and shaken for 2 h. The mixture was then filtered and washed through a Whatman GF/F 70 mm glass microfiber filter with 100 mL portions of Millipore water until no precipitation of chloride as silver chloride (AgCl) was seen upon the addition of silver nitrate (AgNO_3) in the filtrate. The biochar residue was then transferred into a clean 125 mL Erlenmeyer flask along with the filter paper, and 50 mL of 0.5 M barium acetate ($\text{Ba}(\text{OAc})_2$) was added to each flask. The flasks with the mixture were again placed in the shaker set at 120 rpm for 2 h. The mixture was then filtered and washed with 300 mL of Millipore water. The residue was discarded, whereas the filtrate was then titrated with 0.025 M sodium hydroxide (NaOH) solution until the end point ($\text{pH} = 8.2$) was reached. The CEC was then calculated using the following equation

$$\frac{\text{cmol}}{\text{Kg biochar}} = \frac{\text{ml NaOH} \times \text{molarity NaOH} \times 100}{\text{gram sample}} \quad (3)$$

Independent CEC Measurement Using Modified Ammonium Acetate (NH_4OAc) Method (at the USDA/ARS Laboratory). Samples of the biochars (RBC UN and RBC 90D) were sent to the USDA-ARS Laboratory for independent CEC measurements using an ammonium acetate (NH_4OAc) method (Graber et al., 2017) with modifications suggested by Munera-Echeverri et al. (2018).²⁶ Because CEC is pH-dependent, biochar samples were pretreated by adjusting the pH to 7. Briefly, 1 g of dried biochar was mixed with 20 mL of deionized water and shaken horizontally for 4 h at 200 rpm to ensure complete wetting. HCl (1.5 M) (or NaOH) was used to adjust the pH of the slurry to 7. The pH was monitored periodically over 48 h to ensure it had stabilized, and the water was removed by filtration through $2\ \mu\text{m}$ filter paper (Whatman Nucleopore Track-Etch membrane). As a modification of Munera-Echeverri et al. (2018), extraction steps were performed using a filtration apparatus instead of a centrifuge, because the ozone-treated biochar did not form a translucent supernatant. A fresh $2\ \mu\text{m}$ filter and Whatman glass funnel were prepared on a 250 mL Erlenmeyer flask. The pH-adjusted

biochar sample and 20 mL of 1 M NH_4OAc were added to the funnel, swirled, and let to stand on the funnel for 2 h before applying vacuum to remove the NH_4OAc . Repeated additions of 20 mL NH_4OAc were performed for a total of 4 times. For the fourth addition, the NH_4OAc and biochar mixture was left to stand overnight before vacuuming. Next, repeated additions of 20 mL of ethanol (EtOH 100%) were used to remove the noncomplexed NH_4 . EtOH was added to the funnel, swirled to mix with the biochar, and allowed to stand for 2 h before vacuuming. The EtOH wash was performed 4 times. The complexed NH_4 was then displaced with potassium chloride (KCl); 20 mL of 2 M KCl was added to the biochar sample, swirled and allowed to stand for 2 h, and then vacuum was applied to collect the filtrate in an Erlenmeyer flask. A total of four extractions were done, producing 80 mL of extracted volume. Lastly, the ammonium was measured colorimetrically using a microplate reader (Ringuelet et al., 2011), and CEC was calculated as follows

$$\text{CEC (cmol}_c\text{ kg}^{-1}) = \frac{\text{NH}_4^+ \text{ conc (mgL}^{-1}) \times V(\text{mL}) \times 100}{\text{molecular mass of NH}_4^+ \times W(\text{g})} \quad (4)$$

Triplicate samples of each biochar type were measured.

Surface Area Measurement with BET. The surface area was measured for the biochar samples before and after ozonization by using the Brunauer–Emmett–Teller (BET) nova 2000e series instrument. The biochar was weighed (about 0.1–0.3 g) and inserted into the sample cell. The biochar was then vacuum-degassed for 4 h at 150 °C. Helium at 10 psi was used for the backfill. The mass of the degassed biochar was then measured. For the analysis portion, the biochar samples were bathed in liquid nitrogen at 77 K, and the nitrogen pressure was set to 10 psi. The multipoint BET technique was then used to obtain the surface area of the biochar samples. The surface area was measured for both the ground and sieved biochar samples (RBC UN and RBC 90D) as well as the unground biochar samples (RBC UN and RBC 90D) before and after ozonization. For a comparative analysis, the surface area was also measured for a nonozonized ground and sieved biochar from slow pyrolysis (30 min) of pine wood biomass at 400 °C (P400). The same procedure as done for the RBC UN and RBC 90D was used for measuring the surface area of the P400 except that the backfill was done with the adsorbate (here nitrogen) instead of helium. The reason for the change in the backfill gas was as follows: due to the P400 being microporous, the method using helium as a backfill resulted in the inability of the nitrogen gas to adsorb and desorb on the surface, thus resulting in no measurable BET surface area. This may be due to possible entrapment of helium in the micropores of the biochar. To circumvent that limitation, nitrogen gas was used as backfill instead of helium. In order to verify the validity of this method, the ground RBC UN and RBC 90D (before and after ozonization) had their surface areas remeasured with nitrogen as the backfill gas.

Fourier-Transform Infrared (FTIR) Spectroscopy. Biochar FT-IR spectroscopy was analyzed on a Nicolet 6700 FT-IR spectrometer from Thermo Scientific using a pellet. A 1 mg portion of finely ground samples of RBC UN and RBC 90D biochar were mixed with 300 mg of predried and ground FT-IR grade KBr. The FTIR spectra were recorded over the range of 400–4000 cm^{-1} with the resolution of 4 cm^{-1} and 64 scans per sample.

Dissolved Organic Carbon Measurement. The dissolved organic carbon (DOC) concentrations of the filtrates collected from the wash of the dry-ozonized biochar (RBC 90D) and the nonozonized control biochar (RBC UN) were measured using a TOC-Analyzer (Shimadzu TOC-V CPH); the filtrate collection method was described in the section with dry ozone treatment above. Briefly, the DOC concentration was measured from the first wash and the second wash collected from each biochar. The total amount of DOC in mg, extracted from the first and second wash, was combined and divided by the mass of biochar sample in order to get the mg of DOC per gram of biochar. Prior to the measurement, in order to exclude the nondissolved organic materials, the solutions were filtered through a hydrophobic polytetrafluoroethylene (PTFE) 0.2 μm filter

(Millex-FG SLFG025LS). The samples were then diluted at two different concentrations, and the DOC was measured.

X-ray Photoelectron Spectroscopy. Samples of untreated control biochar (RBC UN) and the dry-ozonized biochar (RBC 90D) were sent to the Department of Chemistry in Virginia Tech (Blacksburg, VA 24061) for X-ray Photoelectron Spectroscopy (XPS) analysis. The experimental method is as follows. XPS characterization was performed on a PHI VersaProbe III scanning XPS microscope using monochromatic Al K α X-ray source (1486.6 eV). Spectra were acquired with 100 $\mu\text{m}/100 \text{ W}/20 \text{ kV}$ X-ray and dual-beam charge neutralization over a 1400 $\mu\text{m} \times 100 \mu\text{m}$ area. All binding energies were referenced to C–C at 284.8 eV.

Survey: 280 eV Pass Energy, 1.0 eV/step, 50 ms/step, 10 sweeps; C 1s: 26 eV Pass Energy, 0.1 eV/step, 50 ms/step, 10 sweeps; O 1s: 26 eV Pass Energy, 0.1 eV/step, 50 ms/step, 30–40 sweeps; chemical states of elements were assigned based on the PHI and NIST XPS databases.

Elemental Analysis (Oxygen and Carbon). The ground and sieved nonozonized control biochar (RBC UN) and the dry-ozonized biochar (RBC 90D) samples were sent to the Kumar lab at ODU for Elemental Analysis. It was performed using a FLASH 2000 Organic Elemental Analyzer to determine the oxygen and carbon contents of the biochar samples. In the elemental analysis, the measured mass percentages of oxygen and carbon were converted to molar percentages by dividing the weight percent of each element with its molar mass. The molar O/C ratio was determined by dividing the molar percentages of O with that of C.

Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy. Samples of untreated control biochar (RBC UN) and the dry-ozonized biochar (RBC 90D) were sent to the Nanoscale Characterization and Fabrication Laboratory in Virginia Tech (Blacksburg, VA 24061) for SEM/EDS analysis using an FEI Quanta 600 FEG environmental scanning electron microscope and a Bruker QUANTAX 400 energy dispersive X-ray spectrometer.

RESULTS AND DISCUSSION

Effect of Ozonization on Biochar pH. The biochar pH was drastically reduced as a result of the ozone treatment. The untreated control sample of biochar had a basic pH value of 9.82 ± 0.03 . After 90 min of dry-ozone treatment, the biochar pH dropped down to 3.07 ± 0.03 (Table 1). The decrease in biochar pH is consistent with the understanding that biochar ozonization can create carboxylic acid groups on biochar surfaces, as demonstrated by FT-IR and XPS analyses (see text below). The carboxylic acid groups on biochar surfaces can deprotonate, displaying low pH characteristics as shown in eq 2. To make sure that the acidic pH was not due to any water-

Table 1. pH, CEC, and BET Surface Area of the Ground Biochar before and after Ozonization^a

Parameters	Nonozonized Biochar (RBC UN) (means \pm SD)	Dry-ozonized Biochar (RBC 90D) (means \pm SD)
pH	9.82 \pm 0.03	3.07 \pm 0.03
CEC (cmol/kg) measured by Ba(OAc) ₂ method	17.02 \pm 0.63	152.08 \pm 4.06
CEC (cmol/kg) measured by NH ₄ -OAc method	14.57 \pm 1.62	109.02 \pm 6.33
BET Surface area (m ² /g)	418.3 \pm 17.7	229.2 \pm 6.9

^aThe values are means \pm SD from triplicates ($n = 3$) of measurements for pH, 6 replicates ($n = 6$) for CEC measured by Ba(OAc)₂, triplicates ($n = 3$) for the CEC measured by NH₄-OAc, and 5 replicates ($n = 5$) for the BET surface area measured with N₂ after a backfill with helium.

soluble organic carbon that may be present in the biochar sample after the ozone treatment, the ozonized biochar sample was washed with 300 mL of Millipore water, and the pH for the washed ozonized biochar was measured to be 3.19 ± 0.02 . Therefore, the bulk of the acidifying functional groups upon ozonization were associated with the biochar surface and only a small portion was associated with a soluble component.

Effect of Ozonization on Biochar CEC. Biochar cation exchange capacity (CEC) is a key property central to helping retain soil nutrients, reduce fertilizer runoff, and improve soil water retention. The present experimental study showed that the biochar ozonization can increase the biochar CEC value by a factor of 7–9 (nearly 10). The CEC value of untreated biochar (control) was determined to be 17.02 ± 0.63 cmol/kg using the AOAC Ba(OAc)₂ method. Upon 90 min of dry-ozone treatment, the biochar CEC increased to 152.08 ± 4.06 cmol/kg (Table 1), which to the best of our knowledge represents the highest biochar CEC value experimentally reached so far.

This is a significant result since the improvement of biochar CEC value by ozonization is now far much more than that of our previous study²³ where we demonstrated the increase in the CEC value of biochars by a factor of 2 through ozonization of a pinewood-derived biochar produced by slow pyrolysis at 400 °C (P400).

The Biochar CEC was also independently measured by the USDA team using a somewhat different CEC assay method: the ammonium acetate (NH₄OAc) method following adjustment to pH 7. The measurement with this method also confirmed the increase in CEC upon ozonization of the biochar. As measured with the modified ammonium acetate (NH₄OAc) method, the CEC of the 90 min dry ozonized Rogue biochar (RBC 90D) was determined to be 109.09 ± 6.33 cmol/kg while that of the untreated Rogue biochar control (RBC UN) was measured to be 14.57 ± 1.62 cmol/kg (Table 1). The independent measurement conducted at the USDA laboratory confirmed the same trend in increasing the biochar CEC effected by the ozone treatment. The Rogue biochar is known to have a high surface area. In order to further understand the high increase in cation exchange capacity following ozonization, the surface area was measured on the Rogue Biochar in comparison with that of the P400 biochar.

BET Surface Area. The ground and sieved Rogue biochar samples before ozone treatment (RBC UN) had a surface area of 418.3 m²/g (± 17.7) as reported in Table 1. Compared to the P400 with a measured surface area of only 2.05 m²/g (± 0.42) as seen in Table S4, the Rogue biochar presents a very large surface area; Rogue biochar surface area is 200 times greater than P400 surface area. We believe that the high surface area of the Rogue biochar may make it more favorable to interact with ozone molecules. Therefore, the major difference on biochar CEC improvement between our present and previous studies²³ may be attributed to the difference in BET surface area between the Rogue biochar and the P400.

Upon being ozonized, the ground and sieved Rogue biochar decreased in surface area to 229.2 m²/g (± 6.9) as seen in Table 1. The drop in the measurable surface area upon being ozonized may be due to two factors: (1) It is possible that the ozone is causing the destruction of the pores of the biochar. (2) It is also possible that such a decrease in measurable surface area may be because of the oxygen-rich functional groups created in the micro/nanometer pores of the ozonized

biochar that may in some extent obtrude the pores and/or coat the surface of the biochar. The method of BET surface area measurement uses nonpolar nitrogen gas as the adsorbate. Therefore, these nonpolar gases may be inadequate in terms of giving a true surface area when polar oxygen groups are obtruding the pores and/or coating the surface of the biochar.²⁷

In addition, in order to see the effect of grinding and sieving on the biochar, the surface area was also measured before and after ozonization from the unground biochar materials. The unground nonozonized biochar had a BET surface area of 377.4 (± 22.2) m²/g which is somewhat less than the ground nonozonized biochar control. After ozonization, the measured BET surface area of the unground biochar was 332.1 (± 17.8) m²/g (Table S3). That is, the unground biochar samples also showed a slight drop in the measured surface area after ozonization. However, for the unground biochar samples, the drop in the surface area before and after ozonization is not as significant as it was observed for the ground biochar samples (Table 1). This may be due to the fact that the process of ozonization may have occurred more thoroughly on the ground biochar sample compared to the unground biochar sample.

FT-IR Analysis of Biochar. FT-IR technique was used for the identification and qualitative tracing of functional groups in biochar samples. Overall, FT-IR spectra showed a decrease in aromaticity and increase in carbonyl groups as a result of ozone treatment. Ozone treatment led to an increase in the relative intensity of a broad band centered at 3417 cm⁻¹, which was assigned for the overlap of the H-bonded O–H stretching vibrations of hydroxyl groups from alcohols, phenols, and organic acids and N–H stretching of amine. Bands at 2922 and 3026 cm⁻¹ were assigned for alkyl and aromatic C–H stretching, respectively, and the relative intensity of the alkyl band increased after the ozone treatment (Figure 2a). Bands at 1637 to 1616 cm⁻¹ were assigned for aromatic and olefinic C=C vibrations, C=O in amide (I), ketone, and quinone groups, and the relative intensity of this band increased after the ozone treatment (Figure 2b), which could be due to the increase of the C=O functional groups after ozone treatment. The bands at 1540 to 1560 cm⁻¹ were assigned for COO⁻ asymmetric stretching, which are very weak in the RBC UN, and confirm that the extra carbonyl functional groups are added in the form of carboxylic acid. Two bands at 1494 and 1386 cm⁻¹ were assigned for N–O stretching. The band at 1451 cm⁻¹ was assigned for alkyl C–H bending. The relative intensities of several bands also decreased after the ozone treatment, including three bands at 1115 , 758 , and 471 cm⁻¹ assigned for Si–O stretching and bending. The band at 669 cm⁻¹, which was only present in the RBC 90D, could be due to out of plane ring deformation (Figure 2b).

XPS Analysis of Biochar. The atomic concentration percentages on biochar surfaces measured by X-ray Photoelectron Spectroscopy (XPS) revealed that the ozone treatment caused a 2-fold increase in the amount of oxygen present on the surface of the biochar (Table 2). The atomic percentages on the surface of the biochar were determined from the integrated intensity of the elemental photoemission features corrected by relative atomic sensitivity factors. The survey C 1s and O 1s spectra for the untreated control biochar and the ozonized biochar are shown in Figures S2 and S3. The ozone treatment caused an increase in total O concentration on the surface of the biochar from 13.93% to 23.70% (Table

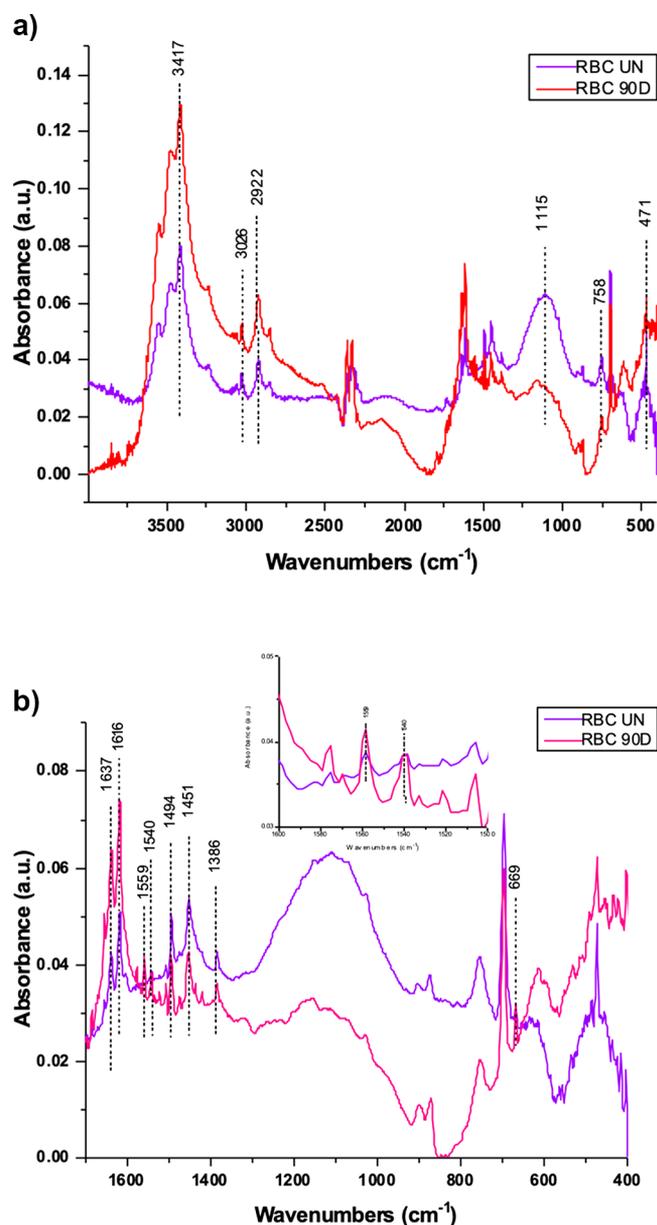


Figure 2. (a) FT-IR spectra from 400 to 4000 cm^{-1} for 90 min dry ozonized Rogue biochar (RBC 90D) and the untreated Rogue biochar (RBC UN) control. (b) FT-IR spectra from 400 to 1700 cm^{-1} for 90 min dry ozonized Rogue biochar (RBC 90D) and the untreated Rogue biochar (RBC UN) control along with an inset from 1500 to 1600 cm^{-1} .

2). The 2-fold increase in the amount of oxygen was mostly seen in the form of organic C=O groups (e.g., carbonyl/carboxyl) and C–O (e.g., hydroxyl/ether) groups. The oxygen content in the form of C=O went from 7.44% for the untreated control biochar to 11.57% for the ozonized biochar. This measurement confirmed our prediction in the installment of the oxygen groups mostly in the form of carboxyl groups. The carboxyl groups observed by XPS here also explain the drop in pH that was shown in Table 1. The oxygen group installment post ozone treatment was also seen in the form of C–O; the untreated control biochar had a C–O of 5.79%, and it increased to 11.33% after ozone treatment (Table 2).

As a result, the formation of oxygen-functional groups including carboxylic acids on biochar surfaces have now, for the first time, been observed with XPS upon biochar surface oxygenation through the ozonization treatment. There is a strong correlation between the biochar oxygen-to-carbon (O/C) ratio and its CEC, due to the negative charge on oxygen functional groups electrostatically attracting cations from solution.^{28,29}

The data in Table 2 showed that the molar O/C ratio ($23.70/76.30 = 0.31:1$) on ozonized biochar surface is indeed significantly higher than that ($13.93/86.07 = 0.16:1$) of the control biochar surface. Therefore, biochar ozonization can indeed be used as a significant biochar surface oxygenation technique.

SEM Imaging and EDS Analysis of Ozonized Biochar.

Scanning electron microscopy (SEM) imaging (Figure 3) showed that the biochar material had little difference before and after the ozonization treatment. This observation indicated that the ozonization process, indeed, did not visibly alter the biochar bulk material appearance as we predicted.

As shown in Figure 3, both biochar samples are fragments of honeycomb-like bulk biochar structure, with particle size <100 μm . There is no noticeable difference in surface morphologies between the RBC UN and RBC 90D. The large variations of particle shape, size, and surface orientation can be used to explain the insignificant changes in O/C ratios obtained by angle-resolved XPS as shown in Table S5 of the Supporting Information.

The Energy-Dispersive X-ray Spectroscopy (EDS) conducted during the SEM imaging showed that the mean O/C ratio value of the ozonized biochar material RBC 90D was 0.16:1, which is slightly higher than that (0.080:1) of the control biochar (RBC UN) as listed in Table 3. The EDS result, which provides “bulk” elemental composition with information depth of >1 μm , shows an increase of O/C ratio of

Table 2. Representation of the Atomic Concentration (in %) from XPS Measurement^a

		Sample								
Ozonized Biochar (RBC 90D)	C							O		
								76.30	23.70	
	sp ² C	sp ³ C	C–O	C=O	CO ₃	C=O	C–O	H ₂ O		
Control Biochar (RBC UN)	C							O		
								86.07	13.93	
	sp ² C	sp ³ C	C–O	C=O	CO ₃	C=O	C–O	H ₂ O		

^aThe atomic percentages represented here were determined from the integrated intensity of the elemental photoemission features corrected by relative atomic sensitivity factors. The survey and C 1s/O 1s spectra are shown in Figures S2 and S3. The data represented here were measured by the Department of Chemistry in Virginia Tech.

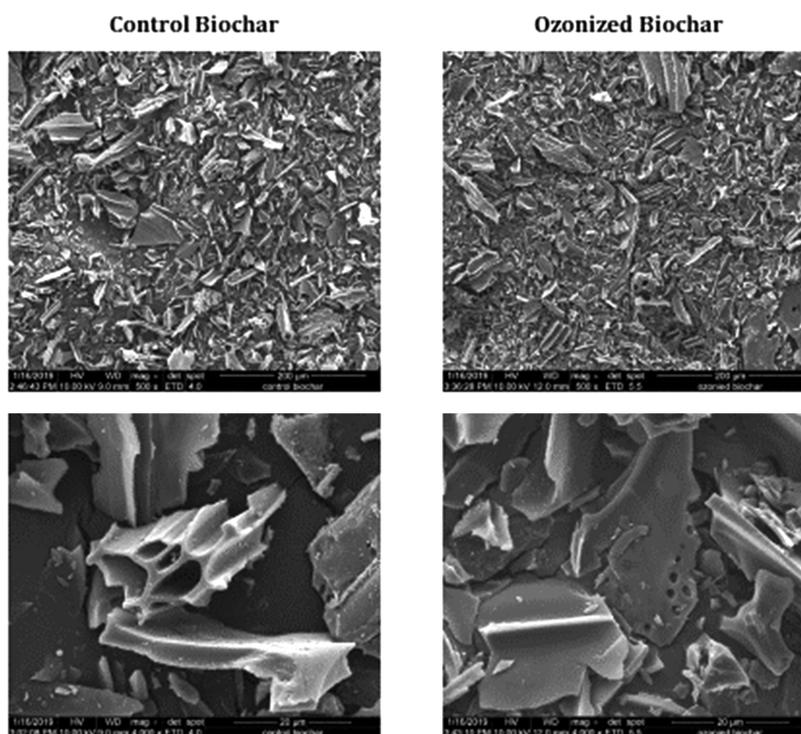


Figure 3. SEM images of the control biochar RBC UN (left) and ozonized biochar RBC 90D (right).

Table 3. SEM-EDS Analysis Result of Ozonized Biochar and Control Biochar^a

Sample	C	O	O/C
Control biochar (RBC UN)	92.26 (± 1.36)	7.74 (± 1.36)	0.080 (± 0.020)
Ozonized biochar (RBC 90D)	86.35 (± 5.21)	13.65 (± 5.21)	0.16 (± 0.07)

^aThe numbers represent mean values (\pm SD) of 20 replicates ($n = 20$) for the control biochar (RBC UN) and 20 replicates ($n = 20$) for the ozonized biochar (RBC 90D).

92.8% (from 0.080 to 0.16) after ozone treatment. This value is about the same as the 94% increase (from 0.16 to 0.31) on the biochar particle surfaces obtained by XPS, which is quite surprising in regarding to the biochar surface oxygenation by ozonization where we expected the effect of ozonization to be noticeable only on the first molecular layer (likely within a few nanometers) of the biochar material surface.

When the specific biochar material RBC UN used in the study is considered, with such a high BET surface area ($418.3 \pm 17.7 \text{ m}^2/\text{g}$), it is so porous at the molecular scales that its averaged carbon material thickness between the porous spaces is only about 5 nm. When such a thin (5 nm) piece of biochar carbon material is oxygenated at its two surface sides by ozone molecules, the resulting surface-oxygenated biochar carbon product may no longer be distinguishable by a comparison of the XPS and EDS measurements on O/C ratio. For example, assuming the thickness of ozonization-enabled biochar surface-oxygenation layer is about 1 nm, it would result in a surface-oxygenated biochar product with a structure of “oxygenated surface layer (1 nm)–biochar carbon layer (3 nm)–oxygenated surface layer (1 nm)” that could no longer be distinguishable by the XPS and EDS measurements on the O/C ratio since the XPS measuring depth could be up to 10 nm. Therefore, the XPS data (Table 2) and EDS data (Table 3)

both showing a doubling of O/C ratio in the RBC 90D sample are still consistent with the understanding that the ozonization process enables oxygenation at the first molecular layer (likely within a few nanometers) of the biochar material surface.

Dissolved Organic Carbon. Ozone treatment resulted in a low pH within its slurry as reported in Table 1. We think that the process of ozonization results in the breakage of C=C double bonds on the biochar material (Huff et al. 2018).²³ Following that breakage, there should be organic carbon fragments of biochar with carboxylic groups “Biochar–COOH” (Huff et al. 2018).²³ In order to further test the efficiency of ozone treatment on our biochar and to verify the formation of those “Biochar–COOH” fragments, the filtrate of the wash of the biochar was collected before and after ozonization for dissolved organic carbon concentration measurement. The effect of ozonization on the biochar was seen on the color of the filtrate extracted from the biochar. The filtrate from the nonozonized biochar appeared clear while the filtrate of the dry-ozonized biochar appeared dark brown thus indicating the presence of more organic carbon fragments (Figure S1). The total extracted DOC (dissolved organic carbon) from the dry-ozonized biochar was $10.98 (\pm 1.00) \text{ mg DOC/g biochar}$ whereas the nonozonized biochar control only resulted in $2.10 (\pm 0.23) \text{ mg DOC/g biochar}$ as reported in Table 4. Biochar ozonization leads to a high amount of dissolved organic carbon in its filtrate which is due to the oxygenation occurring on its surface leading to a breakage of the C=C double bonds.

This result demonstrated that biochar ozonization can also produce certain amount of oxygenated biochar molecular fragments, which may be solubilized by liquid water as DOC for certain special applications such as the unlocking of phosphorus from insoluble phosphate materials in soils.³⁰

Elemental (Oxygen and Carbon) Composition Analysis. In an attempt to characterize the elemental atomic

Table 4. Amount of Dissolved Organic Carbon (DOC) Material Extracted from the Non-Ozonized Control Biochar and the Dry-Ozonized Biochar^a

Biochar Sample	DOC from Biochar (mg DOC/g biochar)
Nonozonized biochar control RBC UN	2.10 (± 0.23)
Dry-ozonized biochar RBC 90D	10.98 (± 1.00)

^aThe values are means \pm SD ($n = 2$).

content of the Rogue biochar before and after ozonization, elemental analysis was performed. Prior to ozonization, the biochar had a high content of carbon (87.022 mol % \pm 5.676) as reported in Table 5. Following ozonization, the carbon

Table 5. Elemental Analysis (Oxygen and Carbon) on the Non-Ozonized and Dry-Ozonized Rogue Biochar Samples^a

	Nonozonized Biochar (RBC UN)	Dry-ozonized Biochar (RBC 90D)
Oxygen mol % (\pm SD)	6.669 (± 1.301)	13.926 (± 1.590)
Carbon mol % (\pm SD)	87.022 (± 5.676)	72.229 (± 0.912)
O/C mol ratio	0.077	0.193

^aThe values are moles average percentages from 6 replicates \pm SD. The weight percent of each element was converted to mole percent by using the respective molar mass of each element. The O/C mol ratio was calculated from the averages of moles percentages of O and C.

content dropped to 72.229 mol % (± 0.912). In addition, following ozonization, there was a significant increase in oxygen content; the nonozonized control had 6.669 mol % (± 1.301) of oxygen whereas the ozonized sample had 13.926 mol % (± 1.590) of oxygen. The molar percentages of carbon and oxygen were used to calculate the molar O/C. The ozonization process increased the molar O/C ratio by a factor of 2.5; the nonozonized control had a molar O/C ratio of 0.077 whereas the dry-ozonized sample had a molar O/C ratio of 0.193 (Table 5). Ozone treatment changed the molar percentages of oxygen and carbon in the Rogue biochar. Even though we did not expect the bulk properties of the biochar to be affected by ozone treatment, those results suggest that dry-ozone treatment may have altered the overall oxygen content of the biochar, as we observed with the SEM-EDS data (Table 3). To test the hypothesis that ozonization mostly happens on the surface of the biochar, we compared the changes in bulk properties before and after the ozonization of a high surface area biochar (Rogue Biochar) and a lower surface area biochar. Previously, in our lab, using P400 biochar, Huff et al. (2018)⁹ demonstrated that the bulk properties of the biochar did not vary as much following ozonization as we believed that the ozonization mechanism happened on the surface of biochar. In an attempt to explain this change in bulk properties, we measured the surface area of P400; we found that P400 biochar has a much smaller surface area (only 2.05 ± 0.42 m²/g) compared to the Rogue biochar (389.9 ± 10.3 m²/g) as measured using nitrogen as backfill following the evacuation procedure (Table S4). Therefore, we believe that the total oxygen groups installed on the surface of the Rogue biochar may be significant enough to slightly change the overall percentage of oxygen within the whole biochar sample, because of its exceptionally large BET surface area so that its averaged carbon material thickness between the porous spaces is only

about 5 nm. When such a 5 nm thin piece of biochar carbon material is oxygenated on its surfaces, the surface oxygenation may now become measurable even with bulk biochar elemental (O and C) composition analysis. Therefore, the experimental results here are still consistent with the technology concept²⁴ that ozonization mostly happens on the biochar surfaces.

Comparison of Surface Oxygenation Methods. The ozone treatment described here has promising advantages over previous work to enhance biochar CEC, particularly when applied to biochars with large surface areas. Prior approaches have included treatment with concentrated hydrogen peroxide, which resulted in a doubling of CEC (Huff and Lee, 2016);³¹ air oxidation of the biochar surface at 250 °C after pyrolysis also increased CEC by no more than a factor of 2 (Suliman et al., 2016);³² previous applications of ozone achieved a similar magnitude of CEC increase. For instance, Smith et al. (2015)³³ reported CEC increases of up to just about 20 and 7 cmol kg⁻¹ for biochars produced from 500 °C pyrolysis of Douglas fir bark (DFBC) and Douglas fir wood (DFWC), respectively. Our previous study²³ demonstrated the increase in CEC value of a pinewood-derived (P400) biochar through an ozone treatment from 15.39 cmol kg⁻¹ (± 1.59) to 32.69 cmol kg⁻¹ (± 2.51), which is approximately 1/4th of the increase reported here. In addition to our effort in optimizing the biochar ozonization process, the major factor that contributed to the present success in producing such a super high cation exchange capacity biochar (109–152 cmol/kg) appeared to be the special characteristics of the Rogue Biochar with its BET surface area of about 400 m²/g (Table 1); whereas the P400 biochar used in our previous study²³ had a BET surface area of only about $2.05 (\pm 0.42)$ m²/g (Table S4). The large surface area of the Rogue Biochar seems to be beneficial to its interaction with ozone molecules for surface oxygenation to achieve greater increase in biochar CEC value.

CONCLUSION

Through this experimental study, we have now demonstrated an improvement of biochar CEC value by a factor of nearly 10 through biochar surface oxygenation by ozonization. The CEC value of the untreated biochar was measured to be anywhere between 14 and 17 cmol/kg. A 90 min dry ozonization treatment resulted in an increased biochar CEC value of 109–152 cmol/kg, which is now almost comparable to that of certain humic materials such as humins.^{34–39} Simultaneously, the biochar ozonization process resulted in the reduction of biochar pH from 9.82 to as low as 3.07, indicating the formation of oxygen-functional groups including carboxylic acids on biochar surfaces. Using the techniques of X-ray photoelectron spectroscopy, the formation of oxygen-functional groups including carboxylic acids on biochar surfaces have been observed upon biochar surface oxygenation through the ozonization treatment. The molar O/C ratio (23.70/76.30 = 0.31:1) on ozonized biochar surface as analyzed by XPS is indeed significantly higher than that (13.93/86.07 = 0.16:1) of the control biochar surface. Similarly, the elemental analysis data showed an increase in O/C mol ratio from the control biochar (0.077) to the dry-ozonized biochar (0.193). The surface area measurements showed a decrease in BET surface area following ozone treatment with values of 418.3 m²/g \pm 17.7 (for the nonozonized control biochar) and 229.2 m²/g \pm 6.9 (for the dry-ozonized biochar). FTIR analysis also showed an increase in the content of oxygen-functional groups in the form of carbonyl groups on biochar surfaces upon ozonization,

which can also produce a certain amount of oxygenated biochar molecular fragments that may be solubilized by liquid water for greater effects upon the application of biochar in soil.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b03536.

Characteristics of Rogue biochar, dissolved organic carbon, BET surface area, XPS angle resolved atomic concentration, SEM-EDS analysis, elemental analysis data of carbon and oxygen, picture of biochar filtrate and XPS spectra (PDF)

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G.K. performed the ozone treatment, FTIR measurement, pH measurement, certain CEC measurements, and wrote a portion of the manuscript. O.S. performed certain CEC measurements, the BET measurement, the DOC measurement, and wrote a portion of the manuscript. X.F. and J.R.M. conducted the XPS and EDS analyses on the biochar samples at Virginia Tech and wrote a part of the manuscript. C.P. and K.T. performed the independent CEC measurement on the biochar samples in their USDA lab and wrote a part of the manuscript. S.K. conducted the elemental analysis measurements. J.W.L. conceived the original concept of biochar surface oxygenation through ozonization, conducted this research project, and finalized the manuscript.

Author Contributions

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Notes

The authors declare no competing financial interest.

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