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Research article

Biochar-surface oxygenation with hydrogen peroxide

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A R T I C L E I N F O

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A B S T R A C T

Biochar was produced from pinewood biomass by pyrolysis at a highest treatment temperature (HTT) of 400 °C. This biochar was then treated with varying concentrations of H_2O_2 solution (1, 3, 10, 20, 30% w/w) for a partial oxygenation study. The biochar samples, both treated and untreated, were then tested with a cation exchange capacity (CEC) assay, Fourier Transformed Infrared Resonance (FT-IR), elemental analysis, field water-retention capacity assay, pH assay, and analyzed for their capacity to remove methylene blue from solution. The results demonstrated that higher H_2O_2 concentration treatments led to higher CEC due to the addition of acidic oxygen functional groups on the surface of the biochar, which also corresponds to the resultant lowering of the pH of the biochar with respect to the H_2O_2 treatment. Furthermore, it was shown that the biochar methylene blue adsorption decreased with higher H_2O_2 concentration treatments. This is believed to be due to the addition of oxygen groups onto the aromatic ring structure of the biochar which in turn weakens the overall dispersive forces of $\pi-\pi$ interactions that are mainly responsible for the adsorption of the dye onto the surface of the biochar. Elemental analysis revealed that there was no general augmentation of the elemental composition of the biochar samples through the treatment with H_2O_2, which suggests that the bulk property of biochar remains unchanged through the treatment.

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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

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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 H_2O_2 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 N_2 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 min. After 30 min had elapsed, the reactor was cooled using an internal water coil, while the biochar was kept under a flow of N_2 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% ± 0.633 of the biomass was converted into biochar through pyrolysis by mass.

Before further use, 50 g 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 1 g 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 h at 110 rpm. After 2 h of shaking had elapsed, each sample was then filtered through Fisherbrand® P8 filter paper and rinsed with 3 × 100 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-g aliquot of each sample in 10 mL of Millipore water in 20 mL screw-top flasks. The samples were then shaken for 1 h 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 can be found in the Supplemental information (SI).

3.2. Biochar cation exchange capacity measurement

CEC measurements were carried out according to a modified AOAC method 973.09 (Rippy and Nelson, 2007) Full details of this protocol can be found in the SI.

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). Full details of this protocol can also be found in the SI.

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 h 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 min. 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).

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

Q_e is the amount of methylene blue removed from solution as

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