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Comparative analysis of pinewood, peanut shell, and bamboo biomass derived biochars produced via hydrothermal conversion and pyrolysis

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ABSTRACT

Biochars were produced from pinewood, peanut shell, and bamboo biomass through hydrothermal conversion (HTC) at 300 °C and comparatively by slow pyrolysis over a temperature range of 300, 400, and 500 °C. These biochars were characterized by FT-IR, cation exchange capacity (CEC) assay, methylene blue adsorption, as well as proximate and elemental analysis. The experimental results demonstrated higher retained oxygen content in biochars produced at lower pyrolysis temperatures and through HTC, which also correlated to the higher CEC of respective biochars. Furthermore, all types of biochar studied herein were capable of adsorption of methylene blue from solution and the adsorption did not appear to strongly correlate with CEC, indicating that the methylene blue adsorption appears to be dependent more upon the non-electrostatic molecular interactions such as the likely dispersive $\pi-\pi$ interactions between the graphene-like sheets of the biochar with the aromatic ring structure of the dye, than the electrostatic CEC. A direct comparison of hydrothermal and pyrolysis converted biochars reveals that biochars produced through HTC have much higher CEC than the biochars produced by slow pyrolysis. Analysis by FT-IR reveals a higher retention of oxygen functional groups in HTC biochars; additionally, there is an apparent trend of increasing aromaticity of the pyrolysis biochars when produced at higher temperatures. The CEC value of the HTC biochar appears correlated with its oxygen functional group content as indicated by the FT-IR measurements and its O:C ratio.

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 min) 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 °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 (200–300 °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 (Hu 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

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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 wells 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 h 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 N_2 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 min 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 $^\circ C\ min^{-1}$ and held at autogenic pressure conditions for 30 min. 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 125 mL 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 (358560 N latitude, 888430 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 0.010 M H_2SO_4 by half units until a final pH of 5.0 was reached. At each half point pH unit, successive CEC measurements were taken. The detailed procedure for CEC measurement is given in the supporting information.

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 50 mL centrifuge tubes. To each biochar sample, aliquots of 30 mL 20 mg/L methylene blue solutions were added. These samples (in 50 mL 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 × 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