Environmental Pollution 179 (2013) 146–152

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Simulated degradation of biochar and its potential environmental implications

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ARTICLE INFO

Article history:
Received 29 October 2012
Received in revised form
8 April 2013
Accepted 15 April 2013

Keywords:
Biochar
Simulated degradation
Surface properties
Environmental implications

ABSTRACT

A simulated oxidation technique was used to examine the impacts of degradation on the surface properties of biochar and the potential implications of the changes in biochar properties were discussed. To simulate the short- and long-term environmental degradation, mild and harsh degradation were employed. Results showed that after mild degradation, the biochar samples showed significant reductions in surface area and pore volumes. After harsh degradation, the biochar samples revealed dramatic variations in their surface chemistry, surface area, pore volumes, morphology and adsorption properties. The results clearly indicate that changes of biochar surface properties were affected by biochar types and oxidative conditions. It is suggested that biochar surface properties are likely to be gradually altered during environmental exposure. This implies that these changes have potential effects for altering the physicochemical properties of biochar amended soils.

1. Introduction

Biochar is a form of black carbon (C) produced by heating biomass in a low or zero oxygen environment. There is no clear-cut boundary between black C and biochar, the term 'black carbon' is often used synonymously with the term 'biochar' in the literature (Nguyen and Lehmann, 2009; Keiluweit et al., 2010; Zimmerman, 2010). Black C is the term for the continuum of C forms, regardless of the production purpose (e.g., naturally produced or deliberately manufactured for energy, fuel or C sequestration) or source of material (e.g., fossil fuels or biomass) (Goldberg, 1985; Schmidt and Noack, 2000). On the other hand, biochar is pyrolysed organic matter created specifically for C sequestration or soil quality improvements (Lehmann et al., 2006). For the purpose of this paper, we will use biochar to describe the solid residues producing by thermal decomposition of biomass under oxygen-limit conditions.

Biochar has received widespread attention from environmental chemists for its ability to enhance soil fertility, adsorb contaminants and sequester atmospheric C in terrestrial systems to offset C emissions and combat global climate change (Yang and Sheng, 2003; Lehmann et al., 2003, 2006,2008; Nguyen and Lehmann, 2009). However, there is a little information on the stability of biochar in the environment, which is fundamental if we are to understand the role that biochar may play in reducing environmental pollution or how it can be used to improve soil fertility. Due to its high aromaticity, biochar is highly stable and can persist in the environment over long periods of time (Goldberg, 1985; Schmidt and Noack, 2000; Skjemstad et al., 2002; Lehmann, 2007). Accordingly, the ^{14}C ages of biochar (referred as black carbon in the literature) were found to lie between 1160 and 5040 years (Schmidt et al., 2002).

Even though biochar appears to be relatively recalcitrant, it must ultimately mineralize. Otherwise, soil organic C would be dominated by accumulated biochar over geological time scales (Goldberg, 1985). Furthermore, an increasing number of observations suggest that biochar can be degraded, by both biotic and abiotic processes (Hamer et al., 2004; Cheng et al., 2006, 2008; Guggenberger et al., 2008). Biological mineralization of biochar has been investigated through incubating biochar with sand, soil, inoculum solution, or nutrients (Hamer et al., 2004; Cheng et al., 2006; Cheng and Lehmann, 2009; Hilscher et al., 2009; Nguyen and Lehmann, 2009; Zimmerman, 2010). On the other hand, to investigate the degradation of biochar, many researchers have used different chemical oxidants, such as oxygen (Toles et al., 1999), acidified potassium dichromate (Ascough et al., 2011), nitric acid

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http://dx.doi.org/10.1016/j.envpol.2013.04.030

(Kamegawa et al., 1998; Moreno-castilla et al., 2000), ozone (Kawamoto et al., 2005) or air alone (Cheng et al., 2006). These studies focused on different aspects biochar stability. For example, biotic and abiotic oxidation processes were compared (Cheng et al., 2006), and half-life or susceptibility of biochar have been investigated (Kawamoto et al., 2005; Zimmerman, 2010; Ascough et al., 2011). These previous studies showed that incubations of biochar at around 30 °C produce mild degradation, which could represent the short-term environmental degradation. Conversely, strong chemical oxidants (e.g., concentrated nitric acid) can harshly oxidize biochar. This kind of oxidation may not occur in the initial phase of biochar environmental exposure, but the changes in the biochar properties provide a basis for investigating the long-term stability of biochar, since it is a challenge to study the long-term environmental degradation of biochar directly.

There remains little information on the effects of environmental degradation of biochar over time, with respect to surface structural characteristics and adsorption properties, in particular. To investigate the variation in biochar surface properties, we used an aerobic incubation at 30 °C (mild degradation) and concentrated nitric acid (harsh degradation) to simulate the short- and long-term environmental degradation, respectively. Therefore, our objectives were to (1) examine the impacts of the simulated short- and long-term environmental degradation on biochar surface properties, and (2) discuss the potential environmental implications of the changes in the biochar properties caused by the simulated degradation.

2. Materials and methods

2.1. Production of biochar

Biochar was produced form three biomass types: the living branch portion of ten-year-old oak (*Quercus phillyraeoides*), three-year-old bamboo (*Phyllostachy edulis*) and the harvested rice (*Oryza stativa*) straw residues obtained from Huajiachi campus, Zhejiang University, Hangzhou, China. The branches of oak and bamboo were collected in the fall in Tianmu Mountain, Linan, Zhejiang Province, China. The straw and branch were air-dried at room temperature and cut into <2 cm pieces. These materials were then placed in ceramic pots, each covered with a suitable lid, and pyrolysed under oxygen-limited conditions in a muffle furnace. The furnace was set to a heating rate of approximately 10 °C min^{-1}, and then held at 350 °C for rice straw and 600 °C for oak and bamboo for 2 h. After pyrolysing the biochar samples were allowed to cool to room temperature. These conditions were chosen to represent natural fires, in which the litter layer temperatures are often around 300 °C, elsewhere temperatures might reach 600 °C (Pyne et al., 1996). The charred biomass materials were milled to pass a 0.15-mm sieve and stored in a desiccator. The resulting samples are referred to as oak-C, bamboo-C and straw-C, respectively.

2.2. Basic properties of biochar

The basic physical and chemical properties of biochars were displayed in Table S1. It revealed that yield, ash, N%, H%, O% and water holding capacity in rice-straw derived biochar were highest, while pH, C% and surface area were lowest.

2.3. Experimental design

2.3.1. Mild degradation

Mild degradation of biochar was carried out in an aerobic incubation experiment. For each treatment, 10 g of biochar were placed in a 500-mL conical flask. To maintain 50% water holding capacity (Cheng et al., 2006), 2.7, 3.5 and 4 mL sterilized water were added to oak-C, bamboo-C and straw-C, respectively. After adding water, the flasks were incubated at 30 °C. To aerate and keep the water content constant, each flask was opened and its moisture was adjusted every 5 days during the first 100 days and then every 10 days for the duration of the incubation period. All bottles with the materials to be incubated, were sterilized by high temperature (121 °C) and pressure (200 kPa). After 374 of days incubation, the flasks were removed and dried at 70 °C for 48 h. The mild degradation was conducted in triplicate. The mineralized biochar samples are hereafter referred to as oak-CM, bamboo-CM and straw-CM, respectively.

2.3.2. Harsh degradation

Harsh degradation of biochar was conducted with modifications to methods outlined by Moreno-Castilla et al. (1995). The biochar was mixed in a 1:10 weight ratio with concentrated HNO_3 (65%) in flasks. The flasks were heated at 80 °C and shaken at 120 rpm in a water-bath at constant temperature for 48 h. After cooling down to room-temperature, the residues were washed with deionized water to remove nitrates. The harsh degradation was conducted in triplicate. The oxidized samples will be referred to as oak-CH, bamboo-CH and straw-CH, respectively.

2.4. Characterization of biochar

The FTIR spectra of biochar samples were obtained by using a Nicolet Ava Tar370 FTIR spectrometer (Nicolet Instrument Corporation). Surface analysis of biochar was conducted with a VG ESCALAB MARKII electron spectrometer (VG Scientific, East Grinstead, Sussex, U.K.) employing monochromatic Mg Kα X-ray source (1253.6 eV). The surface area and pore volumes of biochar samples were measured by nitrogen adsorption using a TriStarII3020 Micrometritics surface area analyzer. Morphology of the biochar particles were investigated using a Hitachi S-4800 scanning electron microscopy (SEM) at ambient temperature and 5.0 kV, after coating the particles with gold. Specific details of these measurements are found in the Supplementary material.

2.5. Adsorption experiment

To better understand the influence of degradation on the adsorption capability of biochar, nitrobenzene uptake by biochar was conducted in aqueous solution. Nitrobenzene was used as an example, because it is a common contaminant in natural environments, such as air, sediments and surface water (Gatermann et al., 1995; Li et al., 2003; He et al., 2006) and widely used in adsorption studies (Chun et al., 2004; Chen et al., 2008). Biochars (50 mg) and 10 mL of solution containing 50–1500 mg L^{-1} nitrobenzene were placed in 15-mL amber screw cap glass tubes. The tubes were immediately closed with polytetrafluoroethylene-lined screw caps and placed on a rotating shaker and agitated (120 rpm) at room temperature (25 °C) for 24 h. A preliminary study indicated that 24 h was sufficient to reach the apparent equilibrium for nitrobenzene adsorption by biochar. After the establishment of sorption equilibrium, the aqueous solution were filtered through a 0.45 μm cellulose acetate membrane filter paper. Then, the concentration of nitrobenzene in the filtrate was analysed by a UV–vis spectrophotometer at a wavelength of 268 nm. The quantitative amount of adsorbed nitrobenzene was calculated as the difference between the added amount and the amount remaining in the final solution. Each experiment was performed in triplicate under identical conditions, and the average data were reported. Isotherms were expressed as the average amount of nitrobenzene adsorbed by biochar (mg kg^{-1}) at the equilibrium concentration and fitted according to the Freundlich equation ($q_e = K_F C_e^n$, Where q_e is the amount of adsorbate adsorbed per unit mass of biochar at equilibrium in mg kg^{-1}; K_F ($mg^{1-n} L^n kg^{-1}$) is the Freundlich affinity coefficient; n (dimensionless) is the Freundlich linearity index; C_e (mg L^{-1}) is the concentration at equilibrium) (Freundlich, 1928). Blanks containing no sorbents were carried out to ensure that adsorption to glass tubes and degradation of nitrobenzene were negligible.

2.6. Statistical analysis

All experiments were conducted with three replicates. Statistical difference between means were determined according to Tukey's test, and statistical significance was assigned at the $p < 0.05$ level. Statistical analyses was performed using SPSS v.18.

3. Results

3.1. FTIR spectroscopy

The broad peak at 3440 cm^{-1} represented the –OH stretching vibration (Fig. 1) (Guo and Bustin, 1998; Cheng et al., 2006). The bands in the 800–870 cm^{-1} region were attributed to C–H out-of plane deformation (Biniak et al., 1997; Moreno-castilla et al., 2000; Ascough et al., 2011). The peaks at 1060–1100 cm^{-1} region could be assigned to aliphatic ether (C–O) symmetrical stretching (Biniak et al., 1997). The band at 1241 cm^{-1} was due to the aromatic C–O-structures and phenolic –OH stretching (Guo and Bustin, 1998). The band at 1380 cm^{-1} was probably due to the stretching vibrations of $-NO_2$ (Akhter et al., 1984). The 1435 cm^{-1} could be attributed to aliphatic C-H_x bending vibrations (Moreno-castilla et al., 2000; Ascough et al., 2011). The aromatic groups C=C detected at 1600 cm^{-1} (Cheng et al., 2006). The peaks at 1538 and 1718 cm^{-1} represented aromatic ring stretching coupled to highly conjugated carbonyl groups and carboxyl C=O stretching vibration, respectively (Moreno-castilla et al., 2000; Cheng et al., 2006; Ascough et al., 2011).