Science of the Total Environment 618 (2018) 276–283

Contents lists available at ScienceDirect

Science of the Total Environment

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

Thermal air oxidation changes surface and adsorptive properties of black carbon (char/biochar)

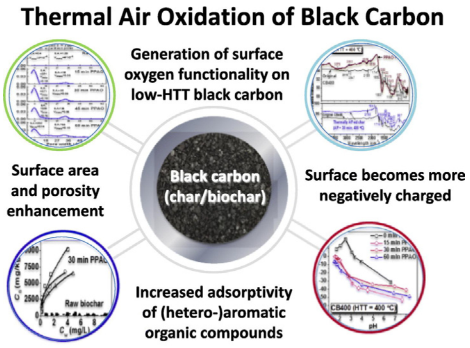
Feng Xiao [a],*, Alemayehu H. Bedane [a], Julia Xiaojun Zhao [b], Michael D. Mann [c], Joseph J. Pignatello [d]

[a] Department of Civil Engineering, University of North Dakota, Grand Forks, ND 58202-8115, United States
[b] Department of Chemistry, University of North Dakota, Grand Forks, ND 58202-9024, United States
[c] Department of Chemical Engineering, University of North Dakota, Grand Forks, ND 58202-7101, United States
[d] Department of Environmental Sciences, Connecticut Agricultural Experiment Station, New Haven, CT 06504-1106, United States

HIGHLIGHTS

- Black carbon (BC) made by thermal air pyrolysis had underdeveloped pore structure.
- Substantial changes were observed by post-pyrolysis thermal air oxidation (AO).
- High-HTT BC showed significant increases in porosity and adsorptivity.
- Low-HTT BC showed moderate increases in these properties after thermal AO.
- Low-HTT BC showed an increase in surface oxygen functionality after thermal AO.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 September 2017
Received in revised form 31 October 2017
Accepted 1 November 2017
Available online xxxx

Editor: Jay Gan

Keywords:
Black carbon
Biochar
Carbon sequestration
Porosity enhancement
Polar functional groups
Environmental sustainability

ABSTRACT

In this study, we systematically investigated the effects of thermal air oxidation on the properties of biomass-derived black carbon (BC) made at carbonization temperatures (HTTs) of 300–700 °C. BC produced by including air in the carbonization step was found to have a low surface area and underdeveloped pore structure. Substantial changes of BC were observed after post-pyrolysis thermal air oxidation (PPAO). Well-carbonized BC samples made anoxically at relatively high HTTs (600 and 700 °C) showed, after PPAO, significant increases in N_2 BET surface area (SA) (up to 700 times), porosity (<60 Å) (up to 95 times), and adsorptivity (up to 120 times) of neutral organic species including two triazine herbicides and one natural estrogen. Partially carbonized BC made at a lower HTT (300 or 400 °C) showed moderate increases in these properties after PPAO, but a large increase in the intensity of Fourier transform infrared spectroscopy bands corresponding to various oxygen-containing functional groups. Well-carbonized BC samples, on the other hand, were deficient in surface oxygen functionality even after the PPAO treatment. Adsorption of the test organic compounds on BC generally trended with BET SA when it was less than 300 m^2/g, but BET SA was poorly predictive of adsorption when it was greater than 300 m^2/g. Overall, our results suggest that thermal reactions between molecular oxygen and BC 1) increase surface oxygen functionality more effectively for low-HTT than for high-HTT BC samples; 2) increase SA and porosity (<60 Å) especially for high-HTT BC samples; and 3) create new adsorption sites and/or relieve steric restriction of organic molecules to micropores, thereby enhancing the adsorptivity of BC. These results will prove useful not only for understanding the fate of environmental BC but also in devising strategies for improving the practical performance of the engineered form of BC (i.e., biochar).

---

* Corresponding author.
E-mail addresses: Feng.Xiao@engr.UND.edu, fxiaoee@gmail.com (F. Xiao).

https://doi.org/10.1016/j.scitotenv.2017.11.008
0048-9697/

1. Introduction

Black carbon is a collective term referring to the carbonaceous residue of combusted or pyrolyzed organic substances. It is widespread in soils and sediments (Schmidt et al., 2001; Czimczik and Masiello, 2007). A major source of environmental black carbon is biomass-derived char formed during natural wildfires and burning practices associated with land clearing and crop residue removal (Skjemstad et al., 1999; Schmidt and Noack, 2000; Skjemstad et al., 2002; Koelmans et al., 2006; Lehmann and Joseph, 2015). During thermal treatment, the lignocellulosic component of the biomass is converted to a porous char structure. Char is generally resistant to both abiotic and biotic degradation depending on the feedstocks and carbonization or pyrolysis temperature (Zimmerman, 2010; Spokas et al., 2014) and therefore represents a relatively long-term sink for carbon (Kuhlbusch and Crutzen, 1995; Glaser and Amelung, 2003). It can be dispersed in the environment by atmospheric circulation and surface runoff (Skjemstad et al., 1999; Schmidt and Noack, 2000; Skjemstad et al., 2002). In some soils, such as the Midwest prairie soils of the U.S., char carbon comprises up to 40–50% of total soil organic carbon (Glaser et al., 2001; Mao et al., 2012).

Biochar, the engineered form of char, has recently attracted attention in the agro-environmental community for its promising beneficial effects as a soil amendment (Godlewska et al., 2017) for improving soil quality (Laird, 2008; Basso et al., 2012; Lehmann and Joseph, 2015), increasing crop productivity (Jeffery et al., 2011), suppressing nitrous oxide (an important greenhouse gas) emissions (Lehmann, 2007b; Woolf et al., 2010), and retaining metal (Cao et al., 2009; Uchimiya et al., 2012; Qian et al., 2013) and organic contaminants (Spokas et al., 2009; Graber et al., 2012; Graber and Kookana, 2015; Kupryianchyk et al., 2016; Kah et al., 2017; Stefaniuk et al., 2017; Zhu et al., 2017). Biochar is also believed to be a sustainable means of carbon sequestration (Woolf et al., 2010; Lehmann and Joseph, 2015). Recent studies have been performed to modify biochar or the carbonization process of biomass in order to enhance the desired properties of biochar (Rajapaksha et al., 2016). These modifications include addition of magnetic properties to biochar (Yang et al., 2016), conversion of biochar to a slow-release fertilizer (Yao et al., 2013), preparation of composites of biochar and nanoparticles (Inyang et al., 2014; Wang et al., 2017a), acid oxidation of biochar (Jin et al., 2017; Vu et al., 2017; Wu et al., 2017), and impregnation of biochar or its feedstock with metal oxides or minerals (Li et al., 2014).

This study introduces thermal air oxidation (AO) as a simple but effective approach to enhance the porosity and adsorptivity of biochar. This process is also very relevant to processes of black carbon formation and fate in soils. The functions and effects of black carbon are determined by surface properties, which, in turn, depend on formation conditions (Kloss et al., 2012; Ronsse et al., 2013). Native, fire-derived char is formed under a wide and fluctuating range of oxygen concentrations. Biochar is typically produced anoxically in order to maximize the yield, but air may be introduced during the process inadvertently or intentionally to reduce energy input (Marsh and Rodríguez-Reinoso, 2006; Gil-Lalaguna et al., 2014) or to cool the reactor (Mahinpey et al., 2009). Char or biochar in soils may also be exposed to hot air during subsequent wild fires, land clearing, or crop residue burning. From January 1 to October 6, 2017, there were approximately 50,283 wildfires in the United States that burned 8.5×10^6 acres (III, 2017). The effects of thermal AO on the properties of char/biochar left or discharged to soils and on the regional and global carbon cycles are potentially profound, but have not been well documented in the literature.

In a recent study (Xiao and Pignatello, 2016), it was found that post-pyrolysis thermal AO (PPAO) of a maple wood char increased its porosity, surface area (SA), surface carboxyl group content, and adsorption of neutral and ionizable organic compounds. The authors proposed that hot oxygen during PPAO reamed pores by removing tarry materials from pores and etching pore walls, resulting in SA and porosity enhancement (Xiao and Pignatello, 2016). They also proposed that the introduced carboxyl groups enhanced adsorption of the ionizable compounds by providing strong charge-assistant hydrogen bonding sites. In that study, the maple wood char was made under inert atmosphere at a single heat treatment temperature (HTT) of 400 °C prior to PPAO at 400 °C in a second step (Xiao and Pignatello, 2016).

In the current study, we investigated the effects of PPAO on the properties of corncob-derived chars made at different HTTs ranging from 300 to 700 °C. The properties and functions of biochar/char depend on its feedstock and carbonization temperature (Lehmann and Joseph, 2015). Previous studies have shown that char made at a HTT of 300 °C is composed mainly of partially altered biomass residues, but char made at 400 °C or above loses most of its lignocellulosic features and consists mainly of polyaromatic structures (Keiluweit et al., 2010; Cao et al., 2012). The lignocellulosic and polyaromatic structures of char may respond differently to thermal air oxidation. In addition, the proportion of cellulose and lignin in the feedstock may be important. Corncob was selected as the feedstock in the present study because it is a common cellulose-rich agricultural residue with a lower lignin content than maple wood used in the previous study (Xiao and Pignatello, 2016) (15% versus 20–30% (Demirbas, 2004, Pointner et al., 2014, Faruk and Sain, 2016)). We also characterized char produced by direct air pyrolysis (AP) where air is present during carbonization. Oxidative pyrolysis has been studied as an approach for reducing the energy input while maximizing the yields of bio-oil and char from biomass (Senneca et al., 2002; Amutio et al., 2012). AP is relevant to the formation of chars in wildfires.

2. Materials and methods

Corncobs were dried in a forced air drying oven (Cascade Tek, Cornelius, OR) at 70 °C for >3 d, ground in a heavy-duty blender, and sieved. Corncob particles between 0.4 and 2 mm were used to produce char (referred as CB) by pyrolysis under a flow of N_2 (200 mL/min) at different heat treatment temperatures (HTTs) (300, 400, 500, 600 and 700 °C) in a dual zone tube furnace (MTI Corporation, CA). The chars were named CBxxx where xxx corresponds to the HTT (°C). The carbonization parameters were selected based on a previous study (Xiao and Pignatello, 2015a). Briefly, corncob particles were heated in the tube at 100 °C for 1 h. The temperature was then increased at a rate of 10 °C/min to the desired HTT at which the corncob particles were carbonized for 2 h. After carbonization, the furnace allowed to cool to 25 °C at 5 °C/min. The yield of CB was calculated on the basis of mass loss. PPAO treatment of CB particles was conducted at 400 °C (within the range of typical wildfire temperatures (Chandler et al., 1983)) in the manner described previously (Xiao and Pignatello, 2016). Briefly, 0.1 g CB particles in a cylindrical shaped aluminum foil tube were heated in a muffle furnace in an air atmosphere (Neytech., Vulcan 3-550, USA). In one experiment, CB samples were produced by heating corncob directly in the muffle furnace at 300 and 400 °C. This process is referred as AP (air pyrolysis). The burn-off of CB during PPAO or AP was calculated by:

$$\text{Burnoff (wt.\%)} = \left(\frac{W_{\text{char/corncob}} - W_{\text{char,PPAO/AP}}}{W_{\text{char/corncob}}}\right) \times 100\%, \tag{1}$$

where $W_{\text{char/corncob}}$ is the weight of the original char or corncob and $W_{\text{char,PPAO/AP}}$ is the weight of char produced by PPAO of char or AP of corncob.

The porosity and pore size distribution of CB particles were measured by means of N_2 porosimetry at 77 K (Autosorb-iQ, Quantachrome, Boynton Beach, FL). Before the measurement, the char sample was outgassed at 493 K under vacuum. The specific SA of char was calculated by the 11-point Brunauer–Emmett–Teller (BET) method. The micro- and meso-porosities and pore size distributions of char were determined by quenched solid density functional theory (QSDFT) from the N_2 adsorption isotherm at 77 K. QSDFT is a state-of-the-art DFT method