Chemosphere 111 (2014) 129–134

Contents lists available at ScienceDirect

Chemosphere

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

Uncovering surface area and micropores in almond shell biochars by rainwater wash

K. Thomas Klasson*, Minori Uchimiya, Isabel M. Lima

U.S. Department of Agriculture, Agricultural Research Service, 1100 Robert E. Lee Blvd, New Orleans, LA 70124, United States

HIGHLIGHTS

- Surface area of almond shell biochar developed at 800 °C at times >120 min.
- Biochar's performance is related to surface area and rainwater alters that property.
- Contacting biochar with rainwater changed the surface area, revealing more pores.

ARTICLE INFO

Article history:
Received 5 December 2013
Received in revised form 11 March 2014
Accepted 12 March 2014
Available online 19 April 2014

Handling Editor: I. Cousins

Keywords:
Biochar
Nitrogen isotherm
Surface area
Washing
Ash
Micropore analysis

ABSTRACT

Biochars have been considered for adsorption of contaminants in soil and water, as well as conditioning and improving soil quality. Pore surface area is an important property of biochar. Biochars were created from shells of two almond varieties with different ash content. The pyrolysis was performed at 650 and 800 °C for 40–240 min. Significant surface areas developed at the higher temperature and at pyrolysis times of 120 min and longer. Washing the materials in synthetic rainwater removed ash and exposed additional surface area, particularly in small-diameter pores. When results from low-ash almond shell biochars were compared with high-ash almond shell biochars, it was found that the pore distribution was more uniform for the high-ash starting material and almost independent of pyrolysis time or washing. The result from the washing study is important as it suggested that adsorptive properties may change once biochars are exposed to rainwater.

Published by Elsevier Ltd.

1. Introduction

Chars from biomass (or biochars) have long been used by humans in agriculture (Lehmann et al., 2003). Charred biomass can help ameliorate plant nutrient availability (Lehmann et al., 2003; Lehmann, 2007) and activated chars can help clean contaminated soil and sediment (Chen et al., 2006; Zimmerman et al., 2008 Uchimiya et al., 2010, 2011, 2012). In a recent review, Lehmann (2007) also made the argument that reversing climate change may be difficult without returning some of the atmosphere's carbon dioxide in the form of char.

The terminology of biochar is relatively new and because of its indented use in agriculture, Joseph et al. (2009) argued that a classification system for biochar is needed. Recently, the International Biochar Initiative (IBI) came out with its standard for biochar classification (Anon, 2013). Both of the resources highlight the importance of biochar surface area and pore structure information. While IBI places the importance of this parameter in Test Category C (optional), Joseph et al. (2009) places a higher degree of importance on the surface properties due to their encompassing affect on water mobility, microbial fauna, and nutrient interactions. The IBI proposes total and external surface area measurement based on an American Society for Materials and Testing (ASTM) method (Anon, 2010). However, there is no consideration given by either of these two resources to what happens if (or when) the material is used and may be in contact with, for example, rainwater. Biochars applied to land will regularly be exposed to rainwater or irrigation water and surface properties may be affected by the water.

The surface area and properties of the biochar can be altered by washing. Klasson et al. (2009, 2010, 2014) showed that biochar washed with weak 0.1 M hydrochloric acid (HCl) had significantly larger BET values than unwashed biochar. Zhang et al. (2013) noted similar results when studying un-activated biochar from (high ash) pig manure. The BET values increased significantly and ash decreased after washing with 1 M HCl as a deashing procedure.

---

* Corresponding author. Tel.: +1 504 286 4511.
E-mail address: thomas.klasson@ars.usda.gov (K. Thomas Klasson).

http://dx.doi.org/10.1016/j.chemosphere.2014.03.065
0045-6535/Published by Elsevier Ltd.

The same trends were obtained for un-activated biochars made with lignocellulosic materials, and the only instance where acid-washing did not increase BET surface area was in the case of biochars made from lignin with very low ash (0.1%) (Klasson et al., 2014). The work presented within addresses the effect of simulated rainwater on surface area and pore structure in biochars created from almond shells.

2. Materials and methods

2.1. Almond shells

Padre variety almond shells were obtained from almonds grown in a research orchard of the San Joaquin Valley Agricultural Sciences Center in Parlier, California. High-ash almond shells (unknown variety) were obtained from a sheller (Bakersfield, California). The materials were ground with a cutting mill (SM 2000, Retsch Gmbh, Haan, Germany) and sieved to retain the 0.84–2 mm portion (No. 10–20 sieve) before pyrolysis.

2.2. Pyrolysis

Raw material (200 g) was placed in a ceramic crucible bowl and pyrolyzed at 650 and 800 °C for 40, 60, 120, 167, and 240 min in a box furnace (Lindberg, Type 51662-HR, Watertown, WI). The average heating rate was not controlled explicitly but was consistently 8–10 °C min^{-1}. Nitrogen (1.6 L min^{-1}) was used as a sweep gas in the furnace to prevent oxygen from entering. After pyrolysis, the material was allowed to cool overnight in the furnace with nitrogen as sweep gas.

2.3. Washing procedure

Some of the pyrolyzed material was washed in synthetic rainwater similar to Method 1312 (Synthetic Precipitation Leaching Procedure) outlined by the US Environmental Protection Agency (Anon, 1994). Synthetic rainwater was created by adding sulfuric acid/nitric acid (60/40 wt%) to distilled-deionized water until the acidity was pH 4.2 ± 0.05. Then rainwater and biochar (20:1 liquid:solids ratio) was combined, placed under vacuum for a minute to force liquid into the pores, and mixed (end-over-end) for 20 h. Following the washing procedure, the content was poured over a 400-mesh screen, briefly rinsed with distilled-deionized water and allowed to dry in an oven (105 °C).

2.4. Surface area

Surface area and pore structure was investigated using a Quantachrome NOVA 2200e nitrogen adsorption system (Quantachrome Instruments, Boynton Beach, FL). Adsorption data were collected using 25 points on the nitrogen isotherm between 0.002 and 0.99 relative pressures at −196 °C (liquid nitrogen). Samples were dried and out-gassed at 200 °C for 3 h under vacuum followed by at least 12 h at room temperature under vacuum. The BET (Brunauer–Emmet–Teller) values and external surface area (as Statistical Thickness Surface Area, STSA) were calculated according to the ASTM D6556-10 method (Anon, 2010; Appendix A) with selected isotherm data points (Thommes et al., 2012) and the differential pore volumes were calculated by taking the derivatives (Klasson, 2008, 2011) of the cumulative pore volume as a function of the pore diameter provided by the NovaWin software package (Version 10.01, Quantachrome). Between 2 and 4 samples (i.e., replicates) from each char preparation were subjected to surface area analysis.

2.5. Ash content

The ash content was determined using a thermogravimetric analyzer (TGA701, LECO Corporation, St. Joseph, MI) and the instrument-adopted proximate analysis method based on ASTM D7582-12 (Anon, 2012). The ash data presented here are on a dry basis. Duplicate analyses of each char preparation were performed.

2.6. Statistical analysis

Mean values were compared between treatments using the recommended Ryan's *Q* (modified) test if variances were equal between treatments or Games–Howell's test if variances were found unequal between treatments (Day and Quinn, 1989). Unless otherwise noted, plus/minus terms listed in text and tables correspond to standard deviations. Further information is located in Appendix A.

3. Results and discussion

The nitrogen adsorption profiles (isotherms) were collected (Fig. A1 in Appendix A) for unwashed and rainwater-washed biochars produced from Padre almond shells. Washing the chars, produced at 120 min and longer pyrolysis times, with rainwater improved the adsorption capacity (volume of N_2 adsorbed) for the same relative pressure (=0.3).

In Table 1, the BET values are listed. Surface BET values of chars created at 650 °C were very low (<2 $\text{m}^2\ \text{g}^{-1}$) when measured on unwashed samples but BET values were significant for some of the unwashed chars created at 800 °C. The dependence of pyrolysis temperature on surface area is well documented. Shenxue (2004) pyrolyzed bamboo at temperatures between 300 and 1000 °C and concluded that, while the optimum temperature for surface area was 700 °C, specific surface areas above 300 $\text{m}^2\ \text{g}^{-1}$ were seen at 500 and 600 °C pyrolysis temperature. In our studies, no significant surface areas were noted at 650 °C pyrolysis temperature. Using a slightly different pyrolysis process than presented here, Chen et al. (2008) pyrolyzed pine needles at several different temperatures between 100 and 700 °C and found significant surface areas at pyrolysis temperatures as low as 400 °C and values increased with increasing temperatures. However, the pyrolysis time was 6 h and they did not look at shorter times as in our case. Karaosmanoglu et al. (2000) investigated pyrolysis temperatures between 400 and 900 °C (for 30 min) and did not show any significant surface area other than at 900 °C in the case of straw and stalks from the rapeseed plant. The surface area creation through pyrolysis is not only dependent on the pyrolysis conditions (temperature and time) but also on the raw material. This was demonstrated by Keiluweit et al. (2010) who pyrolyzed wood and grass at several temperatures between 100 and 700 °C (for 60 min) and found surface areas between 29 and 392 $\text{m}^2\ \text{g}^{-1}$ for wood at pyrolysis temperatures of 400 °C and above, but higher temperatures were needed to create surface area in the case of grass and the surface areas were considerably lower than with wood as a raw material.

Washing the biochars created at 650 °C revealed some additional surface area but it was still below 20 $\text{m}^2\ \text{g}^{-1}$. Unwashed biochars produced at 800 °C with pyrolysis times of 120 min and longer had BET surface areas of 44–423 $\text{m}^2\ \text{g}^{-1}$. When these same chars were washed the BET values increased (Table 1). In general, washing the biochars also exposed some external surface area (STSA) when no such area was detected in unwashed samples.

External surface area (STSA) was not detectable for biochars created at 650 °C or pyrolysis times of 60 min, or less (Table 1). Washing the biochars that already had detectable STSA, did not