



Characterization of narrow micropores in almond shell biochars by nitrogen, carbon dioxide, and hydrogen adsorption



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ABSTRACT

Characterization of biochars usually includes surface area and pore volume determinations by nitrogen adsorption. In this study, we confirmed that there is a substantial pore volume in biochars created via slow pyrolysis from low- and high-ash almond shells that cannot be characterized in this fashion due to the narrow pore sizes. Hydrogen and carbon dioxide were used, in addition to nitrogen, to characterize these narrow micropores. All isotherms, when appropriately normalized, fell on the same characteristic curve which aided in the characterization and understanding of the pore structure. Based on the characteristic adsorption isotherm, the average pore size diameter was estimated to be 0.4–0.8 nm. When washed, the biochars' pore volume increased but the narrow micropore structure remained. While the biochars were alkaline, the pH of the wash solution had no or little impact on the adsorption of CO₂. Overall, the results suggest that N₂ isotherms should be complemented with CO₂ isotherms for proper characterization of biochars. Alignment of such normalized isotherms to characteristic curves can assist in generating a more complete understanding of the pore structure over the entire region of pore diameters.

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1. Introduction

Biochars from biomass have long been used by humans in agriculture (Lehmann et al., 2003). Charred biomass can help improve plant nutrient availability (Lehmann et al., 2003; Lehmann, 2007) and activated chars can provide remediation potential for soil and sediment (Chen et al., 2006; Zimmerman et al., 2008). Biochar soil application has also been discussed as a method of reducing the impact of global warming (Lehmann, 2007; Bracmort, 2009). In order to realize the benefits, Joseph et al. (2009) suggested that a classification system for biochar is needed and the International Biochar Initiative (IBI) recently published its standards for biochar classification (Anon, 2013). Both of the resources highlight the importance of biochar surface area and pore structure information. Joseph et al. (2009) stressed the importance of knowing the pore size distribution of the biochar as macro-pores (>50 nm diameter), meso-pores (>2 nm and <50 nm diameter), and micropores (<2 nm diameter). Biochars with large pore volumes in pores with diameters of >50 nm have a high water holding capacity, while adsorption of small diameter molecules (such as water contaminants) takes place in smaller diameter pores (Joseph et al., 2009).

Biomass chars are microporous and the surface area and pore structure are impacted by raw material, pyrolysis temperature, pyrolysis time, and activation (Chen et al., 2008; Garrido et al., 1987; Jiang, 2004; Karaosmanoglu et al., 2000; Keiluweit et al., 2010; Klasson et al., 2014a,b; Lopez-Gonzalez et al., 1980; Lozano-Castello et al., 2004; McLaughlin and Shields, 2010; Ouensanga et al., 2003; Rodriguez-Reinoso et al., 1984, 1989; Silvestre-Albero et al., 2012). Biochars intended for soil applications will come in contact with rainwater that will alter their surface area properties as a result of ash removal (Klasson et al., 2014b), and it has been shown that ash removal by alkaline or acidic wash increases the specific surface area as measured by nitrogen adsorption (Klasson et al., 2014a,b; Lima et al., 2014; Zhang et al., 2013).

Several gases have traditionally been used for surface area, pore volume, and pore structure characterizations (Brunauer, 1943; Brunauer et al., 1938), and nitrogen (at 77 K) became the gas adsorbate of choice (Sing et al., 1985) and the standard gas for surface area measurements and pore size distribution of some materials (Anon, 2010, 2012). However, it was found that the low diffusivity of N₂ at 77 K and the presence of narrow micropores (or nanopores) in the range of approximately 0.4 nm required a different adsorbate, such as carbon dioxide (at 195 or 273 K), as N₂ cannot penetrate these pores effectively or in a reasonable time period (Marsh and Wynne-Jones, 1964). Some have argued that thermodynamic equilibrium of N₂ in the narrow micropores may take weeks to achieve (Braid

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et al., 2003; Lenghaus et al., 2002). The technique of characterizing materials that has a wide range of pore sizes often requires the use of both N₂ (at 77 K) and CO₂ (at 273 or 298 K) for complete pore size characterization (Cazorla-Amoros et al., 1996; Garrido et al., 1987; Lozano-Castello et al., 2004; Rodriguez-Reinoso et al., 1989). The use of CO₂ as adsorbate has not gone without challenges. While CO₂ does not have a dipole moment, it does have greater electric quadrupole moment than N₂; and CO₂ has shown to interact with oxidized surface groups in molecular interaction simulations of adsorbates and model surfaces (Furmaniak et al., 2009; Tenney and Lastoskie, 2006). The enhanced interaction between CO₂ and surface groups has experimentally been observed by several research groups (Meredith and Plank, 1967; Park and Kim, 1999). Thus, gases with lower (or no) quadrupole moment, such as argon, have been suggested and used (Furmaniak et al., 2009; Jagiello and Thommes, 2004; Silvestre-Alberio et al., 2012) but it should be noted that CO₂ can access smaller-diameter pores than both N₂ and Ar (Braidia et al., 2003) at adsorption equilibrium. Thommes et al. (2012) have provided a recent review of the benefits of each of the methods.

The work presented herein characterizes biochars made from shells of two different almond varieties (with different ash content) and under two different pyrolysis conditions. The biochars were characterized by N₂, CO₂, and H₂ adsorption to determine the extent of narrow micropores. Hydrogen was specifically included as it has a lower quadrupole moment than the other two gases (Orcutt, 1963). The materials were also subjected to water washes to determine if the narrow micropores were impacted by rainwater as well as washing at different pH (Klasson et al., 2014b).

2. Materials and methods

Low-ash (1.0 wt%_{db}) containing almond shells were obtained from San Joaquin Valley Agricultural Sciences Center in Parlier, California, and high-ash (4.2%_{db}) almond shells were obtained from a sheller (Bakersfield, CA). 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 sieves). A commercial activated carbon, Filtrasorb 300, was obtained from Calgon Carbon (Pittsburgh, PA).

Raw material (200 g) was placed in a ceramic crucible bowl and pyrolyzed at 800 °C for 120 or 240 min in a box furnace (Lindberg, Type 51662-HR, Watertown, WI). The heating rate was not controlled but was consistently 8–10 °C/min through the heat-up time. Nitrogen (1.6 L/min) 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. Part of the material was washed with synthetic rainwater using a previous technique (Klasson et al., 2014b) to investigate the impact of rainwater exposure on the material. In addition, one of the biochars was subjected to washing in excess of 48 h with washing solutions adjusted to pH 2, 6, and 10 with HCl before briefly rinsed with deionized water and dried.

Surface area and pore structure were investigated using a Quantachrome NOVA 2200e adsorption system (Quantachrome Instruments, Boynton Beach, FL). Samples were dried and out-gassed at 473 K (200 °C) for 3 h under vacuum followed by at least 12 h at room temperature under vacuum. Adsorption data was collected as 25 points on the nitrogen isotherm between 0.002 and 0.99 relative pressures at 77 K (liquid nitrogen), as 22 points on the carbon dioxide isotherm between 0.05 and 0.99 relative pressure at 273 K (ice water bath), and as 22 points on the hydrogen isotherm between 0.05 and 0.99 relative pressure at 77 K. All isotherms were collected in duplicates and the average values are presented in this manuscript.

Raw isotherms were normalized using the Polanyi theory (Manes, 1998; Polanyi, 1920) as modified by Dubinin (1960), which results in isotherms that correlate the adsorption space (volume, v) used by the adsorbate to the adsorption potential (ϵ) and affinity coefficient (β)

$$v = \text{fn}(\epsilon/\beta) = \text{fn}[(RT/\beta)\ln(p_s/p)] \quad (1)$$

where T , p , and p_s are the temperature, partial pressure, and saturation pressure of the adsorbate. When plotting v as a function of ϵ/β for the gases at different temperatures and pressures on the same sorbent, the resulting curve passes through a common y-axis point, which corresponds to the total space available for adsorption, v_{tot} . We used the relationship between v and ϵ , developed by Dubinin and co-workers (Dubinin, 1989; Dubinin and Astakhov, 1971; Stoeckli, 2001) in the form of

$$v = v_{\text{tot}} \exp\{[B(RT/\beta)\ln(p_s/p)]^n\} \quad (2)$$

also known as the Dubinin–Astakhov (DA) equation in which B and n are constants. By using multiple adsorbates, such as nitrogen and carbon dioxide, a characteristic curve made up by normalized isotherms over a greater range of conditions can be generated (Lozano-Castello et al., 2004). The general use of the relationships as described in Eqs. (1) and (2) to predict adsorptive properties of activated carbons has been summarized by Manes (1998).

3. Results and discussion

The pore characterization method was initially tested with the reference activated carbon. The result of plotting the traditional and normalized isotherms (Eq. (1)) for N₂, CO₂, and H₂ is shown in Fig. 1. As is noted, the total adsorbed N₂ volume significantly exceeded both the adsorbed CO₂ and H₂ volumes under the experimental conditions at all values of p/p_s (Fig. 1A). The total adsorbed H₂ volume exceeded the adsorbed CO₂ volume. Recalculated, using the Polanyi theory, the normalized adsorption data for the three adsorbates followed a general trend line (or characteristic curve) (Fig. 1B), once the affinity coefficients had been applied. The intercept of the curve with the y-axis, represents the total volume (v_{tot}) available for adsorption, which in the case of the reference carbon was approximately 0.4 mL/g (y-axis intercept in Fig. 1B).

The behavior displayed in Fig. 1B has been shown by others for several adsorbates such as N₂, CO₂, benzene, isobutene, and iso-octane (Garrido et al., 1987) and the co-occurrence of the normalized isotherms to a characteristic curve has been noted in the absence of very narrow micropores (Lozano-Castello et al., 2004). Thus, we conclude that the activated carbon in Fig. 1 had an adsorption space accessible to N₂, CO₂, and H₂ without diffusion limitation under the experimental conditions; i.e., very few narrow micropores were noted in the reference carbon.

In Fig. 2, the raw isotherms for N₂, CO₂, and H₂ are shown for the almond shell chars created under different pyrolysis conditions.

As is noted in Fig. 2, the adsorption results using the experimental biochars were significantly different than with the activated carbon (Fig. 1A). The experimental biochars adsorbed more H₂ than N₂ for the same p/p_s . Three of the experimental biochars (Fig. 2A, C and D) adsorbed more CO₂ than N₂. In all cases, both activated carbon (Fig. 1A) and experimental biochars (Fig. 2) adsorbed more H₂ than CO₂. The relatively higher quantities of adsorbed H₂ and CO₂ compared with N₂ are indicative of diffusion limitation of nitrogen into pores that are very narrow (Braidia et al., 2003; Lenghaus et al., 2002). The adsorbed N₂ volume increased approximately five times, while the adsorbed CO₂ and H₂ volumes remained about the same, when the pyrolysis time was doubled in the case of low-ash almond shell biochars (Fig. 2A and B). This suggests the development of pores suitable for N₂ adsorption with extended

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