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Humification characterization of biochar and its potential as a composting amendment

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ABSTRACT

Biochar has received increasing attention due to its applications as a soil amendment. Here, the chemical properties of solid and water-extractable fractions of four biochar samples were investigated. The results showed that wood biochar and bamboo biochar samples were 60%–80% more hydrophobic than those of rice husk biochar and rice husk ash. In addition, the acidity was 3.88 mmol/g from the total functional groups and 1.03 mmol/g from the carboxyl groups/lactones/phenols found in the wood biochar sample, which were about 1.5 times greater than those of the bamboo biochar sample. These functional groups could be used to determine the sorptive capacity of biochar for ionic solutes and water content and to increase the degradation of compost organics. The wood biochar sample was found to have the most humification materials (fulvic acid-like material + humic acid-like material) in the water-extractable fraction, which was 3–10 times higher than that in the rice husk biochar and rice husk ash; humified materials were not detected in the bamboo biochar sample. Humification materials in biochar may be involved in increasing the proportion of humic acid-like materials in humic-like substances within the compost product. Wood biochar had better hydrophobic, sorptive, aromatic, and humification properties compared to other biochars, suggesting that it may be used in composting in order to exert its effect as both a bulking agent and a composting amendment during the solid waste composting process.

Introduction

Biochar is a carbonaceous material formed by pyrolysis of biomass under low oxygen conditions (Lehmann, 2007; Novak et al., 2010). Many types of biomass can be transformed into biochar including wood materials, crop residues, switch grass, organic waste, chicken litter, dairy manure, greenwaste, and wastewater sludge (Chan et al., 2008; Demirbas, 2004; Dias et al., 2010; Hossain et al., 2010; Ogawa and Okimori, 2010; Trompowsky et al., 2005; Yuan et al., 2011). Biochar is widely used as a soil amendment to improve soil properties and enhance plant

yield (Kramer et al., 2004; Liang et al., 2010; Ogawa and Okimori, 2010). Biochar also plays an important role in the formation of humic substances (Brodowski et al., 2005), and has been observed to inhibit the formation or emission of greenhouse gases (Lehmann, 2007). In addition, biochar has been recognized as an effective sorbent for potentially harmful organic compounds and heavy metals in soils and sediments (Chiou and Kile, 1998).

Biochar was recently investigated as a bulking agent in waste composting. Steiner et al. (2011) observed that the addition of pine chip biochar led to increased NH_3 and water-soluble NH_4^+ absorption during poultry composting, as well as decreased nitrogen loss and, therefore, improved compost product quality. Dias et al. (2010) achieved 70% organic matter degradation when poultry manure was mixed with biochar at a 1:1 (W/W) ratio. Jindo et

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al. (2012a) found that the addition of hardwood biochar (10% total weight) to poultry manure and cow manure formed a suitable habitat for microbial growth. Jindo et al. (2012b) assessed the effects of 2% (V/V) addition of wood biochar on poultry manure and different organic wastes and found a 10% increase in carbon content in humic-like substance extraction and a 30% decrease in water-soluble carbon content. The advantages of biochar for composting are generally explained as follows: (1) the aeration and structure of compost materials are improved due to the high nanoporosity and low density of the biochar; (2) development and metabolism of microorganisms are up-regulated due to the porosity and large surface area of the biochar; (3) the high sorption capacity of biochar results in a $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ water-soluble fraction and adsorption of NH_3 , thereby decreasing the loss of nitrogen.

Furthermore, as suggested by soil humification studies (Lehmann et al., 2011; Shrestha et al., 2010) and Jindo et al. (2012b), biochar might also improve composting by regulating the degree of polymerization of the humic-like substances. Therefore, it is necessary to select a suitable biochar for utilization in composting with the goal of strengthening the humification effect. To accomplish this, it is essential to analyze and evaluate the humification characteristics of biochar, especially the biochemical transformations of organic matter that occur in the water-soluble phase. Therefore, investigation of the water-extractable fraction can provide detailed information to enable a better understanding of the properties of biochar. However, few studies have described the humification properties of biochar applied as a composting amendment.

Therefore, this study was conducted to analyze humification material or the humification degree of biochar to test whether humification material in biochar itself is involved in the formation of humic-like substances. To accomplish this, four types of biochar were investigated. Specifically, wood-based biochar was selected because it is the most widely-investigated biochar material (Trompowsky et al., 2005; Dias et al., 2010; Calvelo Pereira et al., 2011; Jindo et al., 2012a, 2012b), whereas bamboo- and rice-based biochars were investigated due to their widespread occurrence in southern China.

1 Materials and methods

1.1 Experimental biochar samples

Three biochar samples collected from fruitwood, bamboo, and rice husk separately were tested, and one rice husk ash was also tested for reference. Commercial biochar samples (Qunfang Gardening Company, China) were prepared and their pyrolysis data from manufacturers showed that the biochar samples were all prepared in kilns. The

wood and bamboo biochars were pyrolyzed at 800–900°C, whereas rice husk biochar was produced at 500–600°C. The different pyrolysis temperatures were due to their wood biomass origin and non-wood biomass origin. The rice husk ash was collected from combustion of rice husk under 500°C. All samples were initially ground and sieved to obtain a particle size of 1 mm, after which they were dried at 65°C for 24 hr and then kept in a dryer for further use.

1.2 Analytical methods

For elemental analysis, the percentage contents of the elements of the biochar samples including carbon, hydrogen, nitrogen and sulfur were measured using an Elementary Analyzer (Vario EL III, Germany), after which the oxygen (%) was estimated as follows: $\text{O}\% = 100\% - (\text{C}\% + \text{H}\% + \text{N}\% + \text{S}\% + \text{ash}\%)$ (Brewer et al., 2011; Calvelo Pereira et al., 2011). The ash contents (%) of biochar were determined by dry combustion in a muffle furnace at 650°C for 2 hr. Three replicates were used for each analysis.

Ground dry biochar samples (<75 μm) were mixed with KBr wafers (sample: KBr = 1:200, W/W) to prepare them for diffuse-reflectance FT-IR measurement (Nicolet 5700, USA) between the wavenumbers of 500 cm^{-1} and 4000 cm^{-1} . The instrument was run with a KBr sample as a blank, and the spectra for all samples were obtained by subtracting the blank.

The oxygen-containing acidic surface functional groups of biochar samples were determined using Boehm's titration method (Boehm, 1994; Chun et al., 2004; Singh et al., 2010). Boehm titration results can be affected by the presence of water-soluble salts and carbonates in biochar, and these components should be removed before the titration (Singh et al., 2010). Briefly, biochar-water mixtures (1:10, W/V) were neutralized to pH 7.0 with HCl, after which they were shaken in a closed container for 24 hr. The biochar was then repeatedly washed until free of Cl^- as detected by AgNO_3 . Next, dried biochar (0.25 g) was mixed with 25 mL of 0.05 mol/L NaOH and 0.25 mol/L NaOH. The suspensions were subsequently shaken in closed containers for 24 hr and then filtered. The filtered basic solution was back-titrated to pH 7.0 with NaOH after acidifying with an excess of HCl solution. The titration process was conducted using an automatic Metrohm instrument (800 Dosino, Swiss). The surface acidity was calculated under the assumption that 0.05 mol/L NaOH neutralizes carboxyl groups, lactones, phenols, and 0.25 mol/L NaOH neutralizes total acidity including carboxyl groups, lactones, phenols, carbonyl groups and any other acidic species.

Biochar samples were shaken with deionized water (1:10, W/V) at 200 r/min for 4 hr on a horizontal shaker at room temperature, after which the pH of the supernatant was measured using a pH meter (pHS-2F, China). The filtrate of samples passed through 0.45 μm polytetrafluo-

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