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Spectroscopic evidence for biochar amendment promoting humic acid synthesis and intensifying humification during composting

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HIGHLIGHTS

- Biochar amendment promoted the neo-synthesis of humic acids during composting.
- Higher *O*-alkyl C/alkyl C ratio and aromaticity of humic acids lead to more intense humification.
- Increases in carboxylic groups of biochar may result from oxidation reactions and sorption of humic substances.

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ABSTRACT

Despite the many benefits of biochar amendment in composting, little information is available about its effects on organic matter humification during the process. In this study the analytical results for two in-vessel composting piles were compared, one amended with biochar (VPSB, pig manure + sawdust + biochar) and the other serving as a control (VPS, pig manure + sawdust). During the 74 days of humification, the increased content of humic acid carbon in VPSB is 16.9% more than that of the control. Spectroscopic analyses show a higher *O*-alkyl C/alkyl C ratio and aromaticity in VPSB at the thermophilic phase, and peak intensities of fulvic-like and humic-like substances were achieved faster in VPSB than VPS. These data inferred that biochar amendment promoted the neo-synthesis of humic acids and intensified the humification of pig manure. Increase in carboxylic groups of biochar as a result of oxidation reactions and sorption of humic substances may correspond to the faster formation of aromatic polymers in biochar-supplemented composting pile. The results suggest that biochar amendment might be a potential method to enhance humification during pig manure composting.

1. Introduction

In recent years, the livestock industry in China has expanded rapidly, bringing with it a surge in the volume of animal waste. According to the National Bureau of Statistics (2010), approximately 3.26 billion tons of animal manure was produced in 2009. If the fecal matter is directly applied to soil, it could pose a hazard in the form of antibiotics or pathogenic microorganisms [1]. As such, utilizing and disposing of this animal waste has become a major issue regarding solid waste management [2]. Composting is a treatment method that is a simple and cost-effective way to stabilize and humify this organic waste under aerobic conditions. It is of considerable economic importance as the resultant compost from livestock wastes can be directly recycled as a marketable organic fertilizer. A better understanding of the transformation and humification of organic matter throughout the composting process is essential for assessing compost maturity, achieving maturity more rapidly and improving quality.

Humification is generally defined as the process of transforming biologically degradable organic matter into a fully stabilized, microbially recalcitrant humic substance. Successful humification of organic matter via composting is frequently a function of the type and quality of the bulking agent [3]. Carbon-rich bulking agents enhance the humification of animal manure and improve the

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quality of the final composts [4]. This is potentially due to modifying the physicochemical properties of initial composting mixtures, thereby providing a suitable environment for microbial activity. The most commonly used materials are chaff, straw and woody by-products, which typically have high C/N ratios. Recently, attention focused on biochar, a carbon-rich material that has been used successfully as bulking agent in poultry manure compost [5]. Previous studies have indicated that bamboo-derived biochar not only improved nitrogen and cation retention, but also lowered the total N_2O emissions from pig manure composting [6–8]. Furthermore, Steiner et al. [9] found that combining compost with biochar effectively remediated contaminated soils and improved soil nutrient retention. Although biochar amendment benefits composting as bulking agents, it is not known whether it enhances the decomposition rate and humification dynamics. Additionally, the mechanism by which biochar stabilizes and humifies pig manure is poorly defined.

Humic substances are usually described as chemically complex and highly heterogenous organic substances comprising large macromolecules with oxidized functional groups [10]. They primarily consist of humic acids (HA), fulvic acids (FA) and humin. Throughout the composting period, microbial degradation lowers the FA and soluble organic carbon content of compost. In parallel, the formation of HA with increasing molecular weight and aromatic characteristics is indicative of a maturing composting [11]. Numerous structural studies have tried to achieve a better understanding of the formation of humic substances. These have been performed using advanced techniques such as ^{13}C nuclear magnetic resonance (^{13}C-NMR) and Fourier transform infrared (FT-IR) spectroscopy [12]. The aromatic content and degree of polycondensation increases, while aliphatic groups and peptide and carbohydrate components decreases with increasing composting maturity. Biochar is a carbonaceous residue of biomass pyrolysis and is highly aromatic. It has a high content of oxidized functional groups, such as C—O and C═O [13], which could be reactive with soluble organic carbon. Additionally, biochar may offer a suitable habitat for microorganisms to attach as it has a strong sorptive capacity due to its high microporosity and large surface area. Jindo et al. [14] suggested that biochar addition could exert an effect on the microbial community, thereby influencing the composting process and the quality of the end product.

In this study, two pilot-scale in-vessel aerobic composting experiments were performed with, or without, biochar. We applied 3D excitation-emission matrix (EEM) fluorescence coupled with ^{13}C-NMR and FT-IR to quantify the changes of chemical composition and structure of the total extractable C (EXC) from samples during the pig manure composting. The primary aim of this study was to investigate the effects of biochar amendment on the dynamics of humification and molecular behavior of HA during composting. We hypothesized that supplementing compost with pyrolytic biochar would affect organic matter decomposition as well as HA structure via chemical interaction with organic matter. Data from this study would provide spectroscopic evidence for the mechanism whereby biochar amendment affected humification during pig manure composting.

2. Materials and methods

2.1. Composting experiments and sampling

Two pilot-scale in-vessel aerobic composting treatments were set up in a suburb of Hangzhou in China and monitored for approximately 12 weeks. Each compost heap consisted of pig manure and bulking agent (sawdust), with one pile receiving the biochar amendment. The two treatments were referred as VPS (in-vessel, 16,500 kg flushed Pig manure + 1540 kg Sawdust), which was effectively the control sample, or VPSB (in-vessel, 16,500 kg flushed Pig manure + 1000 kg Sawdust + 540 kg Biochar), the biochar-amended sample.

Flushed pig manure was collected from local piggery and its main characteristics were: pH (H_2O) = 6.46; water content = 68.2%; EC = 4.52 mS cm^{-1}; and total nitrogen = 33.7 g kg^{-1} dry matter. Sawdust was used as the bulking agent (obtained locally)and its main characteristics were: pH (H_2O) = 6.73; water content = 11.7%; EC = 0.21 mS cm^{-1}; and total nitrogen = 4.3 g kg^{-1}. The bulking agent was milled to a 5 cm particle size, and then homogeneously mixed with pig manure. Biochar, an abundant residue from bamboo processing was purchased from the Yaoshi Charcoal Production Company (Hangzhou, China). The biochar was pyrolyzed at a temperature of 600 °C for 2 h and its main characteristics were: pH (H_2O) = 10.36; water content = 6.1%; C/N = 118; bulk density = 0.40 g cm^{-3}; and specific surface area = 359 m^2 g^{-1}. The compost piles were aerated using natural ventilation and mechanical turning using a tractor-pull windrow turner. Turning frequency varied from 2 to 7 days and was dictated by temperature of the composting windrows. Moisture content of the stock material was initially adjusted to 65 ± 2%, after which there were no further adjustments. The temperature at 30 cm depth below the surface of the compost piles and ambient air was recorded daily with a thermometer.

On day 2, 7, 21, 36, 60 and 81 of composting, six subsamples were removed from six sites of the entire profile spanning the whole profile (from top to bottom) and combined to yield one composite sample. This was then divided into two parts that were both tested in triplicate. One part was immediately stored at 4 °C until analyses, while the other part was air-dried, passed through a 0.25 mm sieve and stored in desiccators until further analyses. Germination index (GI) was measured according to the methods described by Chen et al. [6].

2.2. Extraction of humic compounds

The total extractable C (EXC) was obtained via four 0.1 M sodium hydroxide (NaOH) extractions at a ratio of 1:20 (w/v). The fulvic acid carbon (FAC) was obtained by precipitation at pH 1.0–2.0. The humic acid carbon (HAC) was calculated as the difference between the FAC and the EXC [15]. EXC and FAC fractions were quantified using TOC/TN Analyzer (multi N/C 2100/2100S, Analytik Jena AG).

2.3. Extraction and purification of HA

Humic acids were extracted and purified according to Sánchez-Monedero et al. [16]. Briefly, 10 g of each compost sample, air-dried and crushed, were extracted using 0.1 M NaOH 4 times. Suspended solids were removed via settling and centrifugation (6000 g, 15 min). After centrifuging, the supernatants were carefully aspirated and acidified to pH 1.0 using 6 M HCl and left overnight at 4 °C. The HA precipitates were separated via centrifugation (6000 g, 15 min). The precipitates were purified by dissolving in a minimal volume of 0.1 M NaOH and dialyzed with Spectra Por (1000 Dalton MWCO) to eliminate excess salts and finally freeze-dried (72 h).

2.4. 3D-EEM fluorescence spectroscopy

Samples were filtered (0.45 μm), and diluted to an appropriate concentration. 3D-EEM fluorescence spectra of compost EXC samples and biochar were then obtained by a fluoromax-4 spectrofluorometer (HORIBA, Japan), using a scanning emission fluorescence from 200 to 500 nm at 3 nm increments and the excitation wavelength from 220 to 600 nm at 4 nm increments. The