Molecular markers of benzene polycarboxylic acids in describing biochar physiochemical properties and sorption characteristics[☆]

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ABSTRACT

Biochar function in soil is based on properties such as sorption characteristics, and these are expected to change throughout the life cycle of the biochar. Because biochar particles cannot easily be separated from soil particles, this change is seldom investigated. Biochar-related molecular markers, such as benzene polycarboxylic acids (BPCAs) are promising tools for studying the properties of biochars in complex environmental matrices. In this study, biochars were derived from corn straw and pine wood sawdust at 200—500 °C, and their aging was simulated with NaClO. Biochar properties were characterized by elemental analysis, BET surface characterization and BPCA molecular marker analysis. Chemical oxidation decreased the surface area (SA) but increased the O content of biochars. The oxidation decreased the amount of biochars, with a mass loss in the range of 10—55%. A similar mass loss was also observed for BPCAs and was negatively related to both the pyrolysis temperature and the extent of the condensed structure (higher aromaticity). The biochar amounts were calculated quantitatively using the sum of BPCA contents, with a conversion factor (the ratio of biochar amount to BPCA content) in the range of 3.3 —5.5, and were negatively related to the B5CA content. Three model pollutants, namely, bisphenol A (BPA), sulfamethoxazole (SMX), and phenanthrene (PHE), were chosen to study the sorption characteristics of biochar before and after oxidation. Chemical oxidation generally increased SMX sorption but decreased PHE sorption. The nonlinear factor n, based on Freundlich equation modeling, was negatively related to B6CA for all three chemicals. The BPCA molecular markers, especially B5CA and B6CA, were correlated to the biochar properties before and after oxidation and are thus a potentially useful technique for describing the characteristics of biochar in the environment.

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1. Introduction

Biochar is the product of the incomplete combustion of organic materials and is considered a stable form of carbon that persists in soils over a long period of time (Cheng and Lehmann, 2009; Glaser et al., 2000). Biochar has been given a great deal of research attention in recent years because of its potential benefits in different areas, including soil fertility improvement, contamination remediation and carbon sequestration (Xu et al., 2015). However, it should be noted that the chemical, physical and biological properties of biochar may be subject to change after its application to soil; thus, its environmental roles cannot be evaluated as a steady component. Chemical oxidation is generally used to simulate biochar weathering in soils. Previous studies suggested that biochar aging is mainly a surface phenomenon that alters the interfacial properties and, consequently, sorption properties of contaminants. For example, the formation of hydroxyl, carboxylic and carbonyl functional groups on the surface as well as changes in the particle size and pore size distribution were observed for oxidized biochar, which resulted in the increased sorption capacity for heavy metal ions (Qian et al., 2015). Ghaffar et al. (2015) also noted that the oxidation of biochars increased their sorption to dimethyl phthalate, diethyl phthalate and dibutyl phthalate. Shi et al. (2015) showed that biochar oxidation resulted in an enhanced sorption of paraquat but a reduced sorption of diquat. Obviously, the initial properties of biochar cannot be used to predict its environmental impacts, including its impacts on a contaminant's fate and risk.

To systematically understand its environmental significance, biochar must be monitored continuously in the applied area.

Unfortunately, no practical technique is available to separate bio-char particles from soil particles for quantitative and qualitative analyses. How to describe the properties of biochar in a complex system is thus the major technical barrier for understanding its environmental significance.

Previous studies have reported that black carbon could be measured by molecular tracers, such as the levoglucosan method (Schmidt et al., 1999), analytical pyrolysis (Kaal et al., 2009) and the benzene polycarboxylic acid (BPCA) method (Brodowski et al., 2005; Glaser et al., 1998). BPCAs, as specific molecular bio-markers, can provide both quantitative and qualitative information (Schneider et al., 2010). Briefly, the individual BPCA molecules (such as B3CA, B4CA, B5CA, and B6CA) reflect the size of the aro-matic clusters (Cerqueira et al., 2015; Smittenberg et al., 2012; Vasilyeva et al., 2011). Biochar materials have similar structural units and can thus be described using the BPCA method. This work is specifically designed to study the effects of biochar aging on its properties and contaminant sorption. Biochars were made from corn straw and pine wood sawdust at 200–500 °C. Chemical oxidation by sodium hypochlorite (NaClO) was applied to simulate the aging of biochar in the environment. BPCA molecular bio-markers and common physicochemical properties, such as elemental compositions, surface area, total pore volume and pore size distribution were analyzed for biochars before and after oxidation. Biochar sorption to organic contaminants was also investigated. This study may increase our understanding of the effectiveness of using biochars to adsorb organic contaminants in the natural environment.

2. Materials and methods

2.1. Preparation of original and oxidized biochars

Corn straw (CN) and pine wood sawdust (PW) were collected and oven-dried for 7 d at 70 °C. The pretreated feedstocks were pyrolyzed at different temperatures (200–500 °C) in a muffle furnace. The muffle furnace was provided with continuously flowing N_2 throughout the heating process. After the 4-h charring process, the continuous flow of N_2 was maintained until the tem-perature decreased to 50 °C. The biochars were ground gently and then passed through a 60-mm sieve. All biochars were given a suffix number of 200, 300, 400 or 500 to indicate the pyrolysis temperature, and the original feedstock was given a suffix of Y. For example, CNY refers to the original CN feedstock, and CN200 refers to CN biochar pyrolyzed at 200 °C.

All the biochars were oxidized with NaOCl as described previ-ously (Mikutta et al., 2006). In brief, 20 g of biochar was mixed with 200 mL of 6 wt% NaOCl and reacted for 6 h. Three treatment cycles were conducted at 25 ± 1 °C. To remove residual NaOCl, the oxidized biochars were washed repeatedly with deionized water until reaching a constant pH. The oxidized biochar samples were denoted by CNO or PWO.

All biochars before and after NaClO oxidation were character-ized by their bulk elemental compositions with an elemental analyzer (MicroCube, Elementar, Germany). Two-mg samples were packed and placed into the elemental analyzer. The temperature of the combustion tube for C, H, N, and S analysis was 850 °C. For O analysis, the reduction tube was set at 1150 °C. All analyses were run in duplicate. The surface area, total pore volume, and pore size distribution were measured using N_2 (Autosorb-1C, Quantach-rome) at 77 K. Prior to analysis, samples were degassed for 10 h at 200 °C for biochar and 60 °C for the original feedstocks in a vacuum. Adsorption isotherms of N_2 on biochars were determined in a pressure range of 0.5–101.3 KPa at 77 K (Jagiello and Thommes, 2004; Mukherjee et al., 2011).

2.2. BPCAs analysis

BPCAs were analyzed in the biochars according to Brodowski et al. (2005). First, 20 mg of biochar was digested using 10 mL of 4 M trifluoroacetic acid (TFA) at 105 °C for 4 h to eliminate multi-valent metal. After cooling, the residue was washed several times with deionized water by filtration through a glass fiber filter (Whatman GF/A 1.6 μm) and dried at 40 °C for 3 h. The residue was then transferred to Teflon-lined bombs. Two mL of 65% HNO_3 was added to the bombs and reacted at 170 °C for 8 h in a high-pressure digestion apparatus. Then, the mixture was filtered through an ash-less cellulose filter. Two mL of the digested solution was diluted 5 times with 10 mL of deionized water, and 100 μL of citric acid was added as an internal standard. The solution was filtered through cation exchange resin (Dowex 50 WX8, 200–400 mesh). The treated aqueous samples were freeze-dried and re-dissolved in methanol, and 100 μL of biphenyl-2,2′-dicarboxylic acid in meth-anol was added as a secondary internal standard. These samples were dried using a nitrogen gas stream and subsequently derivat-ized to trimethylsilyl-derivatives for GC-MS analyses (Agilent, 7890A GC equipped with a 5975C quadrupole mass selective detector).

2.3. Adsorbates

Three organic contaminants with distinct properties were ob-tained, as listed in Table 1. Bisphenol A (BPA, $pK_a = 9.59$) is a chemical with functional groups (two phenol groups), but it does not dissociate at the experimental pH level. The chemical morphology of sulfamethoxazole (SMX) depends strongly on the pH. Phenanthrene (PHE) was selected as a hydrophobic organic contaminant without any functional groups. The solubilities of all three chemicals varied from 1.29 to 4052 mg/L, suggesting that these three chemicals represent organic contaminants with very different properties. The BPA was from Sinopharm Chemical Re-agent Co. Ltd., SMX was purchased from Bio. Basic Inc., and PHE was from Acros Organics. All of the other reagents and solvents were higher than analytical grade.

2.4. Batch sorption experiments

Batch sorption experiments were conducted separately for BPA, SMX and PHE on biochars before and after oxidation with NaOCl. Because of the huge difference in their solubilities (Table 1), the sorption experiments were conducted at different initial concen-tration ranges of 1–64 mg/L for BPA, 0.4–40 mg/L for SMX, and 0.1–1.2 mg/L for PHE, at a pH of approximately 7, with a background solution of 0.01 M NaCl and 200 mg/L NaN_3. The batch sorption experiments were conducted in 4–40 mL vials with Teflon-lined screw caps. All vials were shaken continuously on an air-bath shaker for 7 d in the dark at 25 °C. Then, all vials were centri-fuged at 3000 g for 15 min. The supernatants were sampled for adsorbate quantification using high-performance liquid chroma-tography (HPLC). The solid-phase concentrations were calculated by the difference between the initial concentration of BPA, SMX or PXE and the corresponding equilibrium aqueous-phase concentration.

2.5. Quantification of adsorbates

The concentrations of all adsorbates in the supernatants were quantified by an HPLC (Agilent Technologies 1200) equipped with a reversed-phase C18 column (5 mm, 4.6 × 150 mm), and the column temperature was 30 °C, as listed in Table S1. For BPA, the mobile phase was 40:60 (v:v) of acetonitrile and deionized water, the flow