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Effect of aging process on adsorption of diethyl phthalate in soils amended with bamboo biochar

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HIGHLIGHTS

- Biochar amendment significantly enhanced the soil adsorption of diethyl phthalate (DEP).
- Aging can reduce the DEP adsorption to soils treated with biochar.
- The reduction was greater under the alternating wet and dry than that under constantly moist aging process.
- Soil organic carbon content can strongly affect the aging process of biochar.

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ABSTRACT

Biochar is a carbonaceous sorbent and can be used as a potential material to reduce the bioavailability of organic pollutants in contaminated soils. In the present study, the adsorption and desorption of diethyl phthalate (DEP) onto soils amended with bamboo biochar was investigated with a special focus on the effect of biochar application rates and aging conditions on the adsorption capacity of the soils. Biochar amendment significantly enhanced the soil adsorption of DEP that increased with increasing application rates of biochar. However, the adsorption capacity decreased by two aging processes (alternating wet and dry, and constantly moist). In the soil with low organic carbon (OC) content, the addition of 0.5% biochar (without aging) increased the adsorption by nearly 98 times compared to the control, and exhibited the highest adsorption capacity among all the treatments. In the soil with high OC content, the adsorption capacity in the treatment of 0.5% biochar without aging was 3.5 and 3 times greater than those of the treatments of biochar aged by alternating wet and dry, and constantly moist, respectively. Moreover, constantly moist resulted in a greater adsorption capacity than alternating wet and dry treatments regardless of biochar addition. This study revealed that biochar application enhanced soil sorption of DEP, however, the enhancement of the adsorption capacity was dependent on the soil organic carbon levels, and aging processes of biochar.

1. Introduction

Biochar is a carbon-rich solid product produced from the pyrolysis of biomass residues. Application of biochar to soil can improve soil properties (Verheijen et al., 2010). As a recalcitrant carbon-rich material, the application of biochar to soil has great potential to mitigate greenhouse gas emission and sequester carbon (Lehmann, 2007). Past studies have shown that biochar application to soils can decrease the bioavailability of heavy metals and organic pollutants in contaminated soils (Beesley et al., 2011; Zhang et al., 2013). For example, Yang and Sheng (2003) observed that the particulates produced from burning wheat and rice residues were 400–2500 times more effective than soil in sorbing diuron over the concentration range of 0–6 mg L^{-1} in water. High

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specific surface areas and microporous structure make biochar a sorbent for the adsorption of a range of organic and inorganic chemicals. When biochar is applied to the soil, it undergoes a range of biogeochemical interactions and their properties are likely to change with time in soil, a process commonly referred to as "aging" and biochar properties may change during the process of aging (Kookana, 2010). The process of aging can be either abiotic or biotic which can lead to changes in the sorption characteristics of the sorbent. For example, the presence of some metallic ions (e.g. Cu^{2+} and Ag^{+}) and organic compounds with higher hydrophobicity and/or high molecular size can significantly alter surface chemistry and pore network structure of biochar (Chen et al., 2007; Wang et al., 2006). Also, aging processes may introduce functional groups (i.e. carboxylic) to biochar surfaces, thereby impacting its adsorption properties (Qian et al., 2015).

Phthalate acid esters (PAEs) are a class of organic compounds widely used as plasticizers to improve the properties of plastics (He et al., 2015; Fang et al., 2010). Surveys showed worldwide production of PAEs is approximately 6 million tons per year and a large amount of these compounds are released into the air, sediment, natural water, wastewater, and soils (Bauer and Herrmann, 1997; Mackintosh et al., 2006; Shailaja et al., 2007). Recent years have witnessed widespread urbanization around the world, causing a rapid expansion of the peri-urban interface in many cities, especially in Asia (Zeng et al., 2008). In many peri-urban areas in Asia (i.e., in China), land use has been transformed from rice-based to vegetable-based systems (Wang et al., 2013). Therefore, there is likely to be a greater demand for plastic greenhouses and plastic mulch to grow vegetable crops to cope with the increasing demands. The PAEs in the plastic greenhouses, plastic mulch and fertilizers can be potentially released to the soil, resulting in unwanted consequences of soil contamination. In recent years, high levels of PAEs contaminated agricultural soils have already been detected in the Pearl River Delta and northeast China (Xu et al., 2008; Zeng et al., 2008).

Diethyl phthalate (DEP) is one of the most frequently used phthalates possessing high aqueous solubility and is toxic at high exposure levels as well as at low doses for a prolonged period and it may accumulate in the soil and enter the human food chain (Yang et al., 2005; Sun et al., 2012). Both the higher concentrations of DEP and exposure to lower concentrations for a longer period of time could impact human health (Sun et al., 2012). Therefore, it is essential to find an effective way to remediate the soils contaminated with this pollutant.

In our previous study, we suggested that biochar can be used as a sorbent to reduce the bioavailability of DEP in the contaminated soils (Zhang et al., 2014). However, aging process may change the adsorption capacity of biochar. Recently, most studies were focused on the effect of constantly moist aging process on biochar' adsorption capacity. Generally, the alternating wet and dry process is more relevant to the field conditions. The objective of this study was therefore to assess the effect of different aging processes on the adsorption capacity of DEP to the soils amended with bamboo biochar. We hypothesized that different aging processes altered the adsorption ability of biochar for DEP.

2. Materials and methods

2.1. Chemicals, soils and biochar

Analytical standard of diethyl phthalate with a purity ⩾99.5% was obtained from Shanghai Lingfeng Chemical Reagent (Shanghai, China). Stock solution of 400 mg L^{-1} DEP was prepared in methanol and used for analytical purposes. High Performance Liquid Chromatography (HPLC) grade of acetonitrile was obtained from Tedia (Fairfield, Ohio, USA). Other chemicals were of analytical grade.

Two soils differing in organic carbon (OC) contents were collected in November 2012 from a vegetable garden in the suburb of Lin'an near Hu Tangxia village, in Hangzhou, China. The soil samples were collected from the surface with a depth of 0–0.2 m. After air-drying, the soils were passed through a 2 mm sieve. Selected physicochemical properties of soils are shown in Table 1.

Bamboo used to produce biochar was oven dried at 80 °C for 24 h. The stainless steel vessel was constantly purged with dry nitrogen gas at 3.5 L min^{-1} and the vessel was heated over 3 h to a final hold temperature of 820 °C. Physicochemical properties of biochar are shown in Table 2.

2.2. Aging treatments

On the basis of our preliminary investigation, the application rates of bamboo biochar were set at 0.1% and 0.5% (w/w) of soil weight. Soils were mixed with biochars using a soil mixer and were directly used in the sorption and desorption experiments. An additional set of samples, after adjusting the water content of soil to about 70% of maximum water-holding capacity, were equilibrated at 25 ± 1 °C for 30 d to evaluate the effect of aging. The samples were checked daily for water loss by weighing, and appropriate amount of deionized water was added to compensate for water loss when required. Other well-mixed samples were incubated under the same conditions and aging time, and added to compensate for water loss every 10 d (alternating wet and dry).

2.3. Adsorption and desorption experiments

Sorption of DEP by the bamboo biochar was measured by the batch equilibration technique following an earlier protocol (Yu et al., 2006). Briefly, 4 g each of the treated soils was weighed onto a glass centrifuge tube (40 mL) with Teflon-lined screw cap and 20 mL of 0.01 M $CaCl_2$ (the $CaCl_2$ was used to maintain the ionic strength), containing 250 mg L^{-1} of NaN_3 to inhibit microbial activity, was added to obtain an initial solution concentration of 2, 4, 6, 8, and 10 mg L^{-1} of DEP (Yu et al., 2006; Wang et al., 2010). Triplicate samples were prepared for each treatment. For the comparative assessment between different biochar treatments under similar conditions, an equilibrium contact time of 24 h was found to be adequate for the purposes of this study. Tubes were shaken for 24 h, centrifuged at 2191 g for 10 min (Wang et al., 2010), and the supernatant was analyzed for DEP concentrations using High Performance Liquid Chromatography and UV detection. The

Table 1
Selected properties of soils (0–0.2 m).

Soils	Organic carbon (OC) (g kg^{-1})	Total *N* (g kg^{-1})	pH	Electrical conductivity[a] (dS m^{-1})	Clay (%)	Silt (%)	Sand (%)
Low OC soil	3.5	0.3	5.83	0.31	16.9	44.4	38.7
High OC soil	22	2.0	6.04	0.24	16.4	45.0	38.6

[a] Electrical conductivity was measured in 1:5 water.