



Effects of chemical oxidation on phenanthrene sorption by grass- and manure-derived biochars



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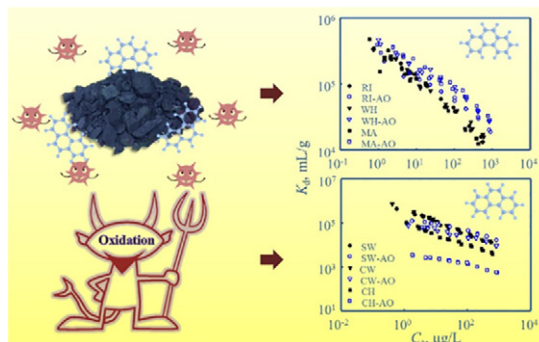
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HIGHLIGHTS

- Phenanthrene (PHE) sorption by grass-based biochars was elevated after oxidation.
- PHE sorption by manure-based biochars was unchanged or attenuated after oxidation.
- Pore-filling and π - π EDA interactions regulated sorption of grass-based biochars.
- Ash removal during oxidation increased sorption sites of manure-based biochars.

GRAPHICAL ABSTRACT



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ABSTRACT

The oxidation of biochar in the natural environment has been widely observed. However, its influence on the sorption of hydrophobic organic compounds (HOCs) by biochars, especially biochars with high contents of minerals, remains poorly understood. In this study, sorption of phenanthrene (PHE) by grass straw-based biochars (GRABs) and animal waste-based biochars (ANIBs) produced at 450 °C before and after oxidation with HNO₃ was investigated. The biochar samples were characterized using elemental analysis, X-ray photoelectron spectroscopy, ¹³C nuclear magnetic resonance, and CO₂ adsorption. Characterization results demonstrate that HNO₃ treatment of biochars caused O enrichment, loss of alkyl C, and rise of aromaticity. The organic C-normalized surface area (CO₂-SA/OC) of both GRABs and ANIBs generally increased after oxidation. The sorption nonlinearity of PHE by the biochars was weakened after HNO₃ treatment. The sorption capacity of PHE by oxidized GRABs was consistently elevated compared with the untreated samples, indicating that the high sorption capacity of PHE by GRABs may be maintained for a long time after being added into soils. By contrast, PHE sorption by ANIBs was unchanged or attenuated after oxidation. Polar groups facilitated the sorption of PHE by GRABs, while inhibited that by ANIBs. Pore-filling and π - π electron donor-acceptor interactions regulated PHE sorption by GRABs. Our results imply that GRABs are promising sorbents for environmental applications in view of their long-lasting sorption capacity.

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1. Introduction

Biochar, a recalcitrant carbon (C)-rich material produced from biomass through pyrolysis under oxygen (O)-limited conditions, has attracted great interests in recent years due to its potential role in C sequestration, climate change mitigation, and soil remediation (Laird, 2008; Lehmann, 2007; Schulz and Glaser, 2012). Biochar has promising characteristics for soil amelioration because of its neutral to alkaline pH, porous structure, high water holding capacity, good biological and chemical stability, and especially, strong affinity for inorganic and organic pollutants (Bian et al., 2014; Cao et al., 2009; Kookana et al., 2011; Sun et al., 2012; Wang et al., 2016). Sorption of hydrophobic organic compounds (HOCs) by biochar can be up to 400–2500 times more effective than that of soil (Yang and Sheng, 2003a). A decisive factor for the successful application of biochar in contaminated land restoration is that whether the high pollutant sorption capacity of biochar is long-lasting after being added into soils.

The recalcitrance of biochar does not mean that the properties of biochar remain unchanged after its deposition. Actually, biochar can be rapidly oxidized in short-term incubations, whereby biochar properties were altered via the formation of O-containing functional groups (Cheng et al., 2006). Biochar C stability varies depending on the proportion of different components (e.g. water-soluble organics, high molecular weight aliphatic moieties, insoluble aromatic structures, and mineral nutrients) and the degree of condensation of aromatic C, both of which are mainly regulated by biomass feedstock and pyrolysis temperature (Kuzaykov et al., 2014; Singh et al., 2012). For instance, the animal manure-based biochars (ANIBs), which had lower concentrations of aromatic C and had lower degrees of aromatic condensation, mineralized faster than the grass straw-based biochars (GRABs) (Singh et al., 2012). Compared with GRABs, the higher abundance of mineral nutrients in ANIBs (Singh et al., 2010) may cause defects in the core biochar C structures, consequently decreasing biochar C stability (Nguyen and Lehmann, 2009; Singh et al., 2012).

Oxidation of biochar in soils has important implications for the fate of HOCs. The alteration of surface properties after oxidation, especially O enrichment in the aged biochars may lead to the change in their sorption affinity towards HOCs. However, current literature still debates on the influence of aging on HOCs sorption to biochars. Some works have shown that aging decreased the capacity of biochars to sorb HOCs (Chen and Yuan, 2011; Cheng et al., 2014; Yang and Sheng, 2003b). Nevertheless, several other studies reported that biochar had a high sorption capacity for HOCs that was maintained during harsh aging (Hale et al., 2011; Jones et al., 2011). Moreover, enhanced sorption of HOCs, including phthalate esters and herbicides, on the oxidized biochars has also been shown (Ghaffar et al., 2015; Shi et al., 2015; Trigo et al., 2014). There are probably two reasons for the inconsistent change trend of sorption capacity of HOCs by biochars after aging. (i) The sorption behavior of oxidized biochar may rely on oxidation approaches. Incubating biochar with soil for a short-term showed no obvious alteration in HOCs sorption by biochar (Shi et al., 2015), probably because biochar C mineralized very slowly in natural environment (Keith et al., 2011). Additionally, biochar is expected to interact with soil components (Kasozi et al., 2010), resulting in the contamination of biochar by natural organic matters (NOM), which show much lower sorption capacity for HOCs than biochar (Yang and Sheng, 2003a). Since it is difficult to separate biochar from non-biochar sources of C aged in biochar-amended soils, the presence of NOM on the surface of oxidized biochars would interfere with the determination of biochar sorption capacity. This differentiation problem can be avoided by using various laboratory methods to artificially oxidize biochars (Hiemstra et al., 2013; Singh et al., 2012). Short-term harsh aging of biochars by chemical reagents has been suggested as an effective way to examine the long-term sorption properties of HOCs by biochars after deposition, because this chemical aging could give hints of hundreds to thousands of years of aging processes in the natural

environment (Hale et al., 2011). (ii) The formation of O-containing functional groups on the oxidized biochars may play multiple roles in HOCs sorption, the net effect of which varying with the molecular structure of solutes and biochars. Apart from the aforementioned weakening of hydrophobicity of biochar surface, the attachment of O-containing groups to the condensed aromatic structures of oxidized GRABs might enhance the π -polarity of surface aromatic rings on the biochar, rendering the formation of strong π -electron donor-acceptor (EDA) bonds between GRABs and aromatic pollutants (Wu et al., 2012). The π - π EDA interactions between ANIBs and aromatic pollutants, however, is unlikely due to the lower degree of aromatic condensation of ANIBs (McBeath et al., 2014), reducing the ability of ANIBs to accept or donate electron. Therefore, the net effect of O-containing functional groups on HOCs sorption by the oxidized ANIBs may be negative.

As mentioned above, it is probably that the O-containing functional groups formed during oxidation will play different roles in HOCs sorption by GRABs and ANIBs, resulting in different sorption properties of GRABs and ANIBs after oxidation. In comparison with GRABs, the effect of O-containing functional groups formed during oxidation on HOCs sorption by ANIBs remains poorly understood. Therefore, in the present study, sorption of phenanthrene (PHE), a nonpolar aromatic compound, to fresh and chemically oxidized GRABs and ANIBs was examined. We hypothesize that PHE sorption by the oxidized GRABs will be enhanced by the O-containing functional groups, formed during chemical oxidation, via strengthened π - π EDA interactions between PHE and oxidized GRABs. In contrast, O enrichment after oxidation will attenuate PHE sorption by ANIBs through increasing the hydrophilicity of biochar surface.

2. Material and methods

2.1. Chemicals and materials

Two kinds of biomass, including grass straws of rice, wheat, and maize and animal manure wastes of chicken, swine, and cow, were collected to produce GRABs and ANIBs, respectively. Grass straws were washed with deionized water before use. The ground feedstocks were carbonized at 450 °C for 1 h under N₂ atmosphere using a muffle furnace. The charring temperature was selected according to the recommended value for manufacturing biochar for soil amendment purposes (Chan et al., 2007; Jones et al., 2012). The holding time (1 h) was also used in previous studies for biochar preparation (Han et al., 2014; Shaaban et al., 2014). The biochars were treated with 0.1 M HCl to decrease pH values of biochars and remove some nutrients, carbonates, and dissolved organic matter (Sun et al., 2013b). The biochars were then flushed with deionized water until neutral pH, freeze-dried, and sieved (<0.25 mm) for further analysis as the original biochars. To obtain the oxidized biochars and investigate their sorption of PHE, all biochars were oxidized with 25% HNO₃ (~5.5 M) at 1:30 solid/liquid ratio. The flasks containing the suspensions were heated under reflux at about 90 °C for 4 h (Hiemstra et al., 2013; Shindo and Honma, 1998). After removal of excess acid by washing and centrifugation, the oxidized biochars were freeze-dried, ground, and stored for subsequent use. Here, the biochar samples were abbreviated as RS, WS, MS, SM, CM, and CHM, respectively, according to the feedstocks (rice straw, wheat straw, maize straw, swine manure, cow manure, and chicken manure). The ¹⁴C-labeled (98 + %) and unlabeled PHE (98 + %) were purchased from Sigma-Aldrich Chemical Co., USA. Other chemicals were purchased from Sinopharm Chemical Reagent Beijing Co., China, at analytical grade. The water solubility (*S*_w) of PHE is 1.12 mg/L (Sun et al., 2012).

2.2. Sorbent characterization

The bulk and surface elemental composition of the fresh and oxidized biochars were determined using elemental analysis (Elementar Vario ELIII elemental analyzer, Germany) and X-ray photoelectron

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