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Adsorption and catalytic hydrolysis of carbaryl and atrazine on pig manure-derived biochars: Impact of structural properties of biochars

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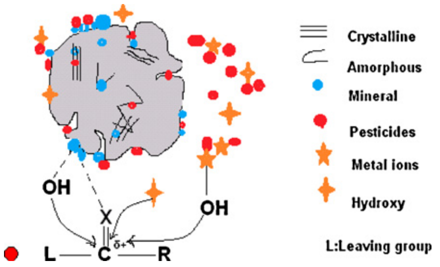
HIGHLIGHTS

- ► High ash content biochar can increase solution pH and released metal ions.
- ► Ash in biochar can combine pesticide through specific interactions.
- ► Composition and structure of biochar is favor for the hydrolysis of pesticides.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochars were produced from pig manure to elucidate the influence of biochars with high ash contents on the fate of pesticides. Adsorption and catalytic hydrolysis of carbaryl and atrazine on original biochars and deashed biochars were investigated. The two pesticides were substantially adsorbed by the biochars, with organic carbon normalized sorption coefficient (K_{oc}) values of $10^{2.65}$–$10^{3.66}$ L/kg for carbaryl and $10^{1.90}$–$10^{3.57}$ L/kg for atrazine at C_e of 0.5 mg/L. Hydrophobic effect alone could not explain the sorption, and several other processes including pore-filling and π–π electron donor–acceptor interactions were involved in pesticide adsorption. Adsorption increased greatly on the deashed biochar, indicating that some organic sorption sites in the original biochars were blocked or difficult to access due to their interactions with inorganic moiety. The pesticides were found to hydrolyze faster in the presence of biochars, and in the presence of biochar pyrolyzed at 700 °C, carbaryl and atrazine were decomposed by 71.8% and 27.9% in 12 h, respectively. The elevated solution pH was the main reason for the enhanced hydrolysis; however both the mineral surface and dissolved metal ions released from the biochars were confirmed to catalyze the hydrolysis.

1. Introduction

Biochar is a carbonaceous material produced from oxygen-limited pyrolysis of biomass [1]. Interest in biochars has recently increased because the application of biochars on farmland has been advocated to provide a means of sequestering carbon and increasing soil fertility [2–4]. Biochars show extraordinarily strong adsorption affinities for contaminants [5–8]. The adsorption of hydrophobic organic chemicals (HOCs) on biochars and other carbonaceous materials has been well documented [5,9,10], with adsorption coefficients (K_d) of 10^3–10^8 L/kg. The highly aromatic and porous structures in biochars, which favor both hydrophobic effect and specific interactions, have been suggested to contribute to the high adsorption coefficients [11,12].

Until now, the majority of studies concerning the adsorption of organic chemicals have been limited on biochars derived from plant residues [13–17]. Plant-derived biochars commonly contain low amounts of inorganic moiety (ash), so the effect of ash on HOC adsorption has usually been neglected. Livestock

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manure is an important agricultural waste biomass, and using such manure to produce biochar is a possible approach to recycling livestock manure [18]. Biochars derived from livestock manures may have quite different compositions compared to those from plant residues. One important difference is that biochars derived from livestock manures usually contain high ash content [19,20]. The high content of ash and its interaction with organic moieties may influence the interactions of biochars with organic pollutants. The influence of the interaction between inorganic and organic moieties on sorption capacity has been extensively studied on natural geosorbents [21,22], with conflictive results. Generally, mineral surfaces inhibit the non-specific adsorption of organic moieties by reducing the accessibility of organic sorption sites [23]; this is particularly true for the partitioning of apolar organics [24]. However, mineral surfaces can also enhance sorption of polar organic chemicals through specific interactions, such as electron donor–acceptor [25] and H-bonding interactions [26]. For ionizable organics, they may provide sites for additional interactions of cation or anion binding. Though these mechanisms have been proposed previously, the influence of biochars of high ash content on the fate of organic pollutants has seldom been studied [27–29].

Pesticides are common soil pollutants. Adsorption on biochars has been studied for some pesticides, such as diuron [30], triazine [31], and dieldrin [32]. Though the adsorption capacity of biochars for polar pesticides was not as large as those for apolar HOCs [33], biochars are generally good adsorbents for pesticides, with K_d values ranging between 10^1 and 10^3 L/kg [30–32]. Hence, the application of biochars to soils can have great impact on the fate of pesticides. Moreover, modern pesticides are designed to be easily degraded. Hydrolysis is an important mechanism for abiotic degradation of pesticides. Many factors influence pesticide hydrolysis, which include the pH, dissolved ions as well as the presence of clay and metal oxides that can catalyze the hydrolysis reaction [34–36]. Manure-derived biochar contains a high ash content, which is expected to influence the hydrolysis of pesticides. However, there is no prior study on this aspect of biochars.

The objective of this study was to obtain a thorough understanding about the effects of biochars with high ash content on the fate of pesticides. Two biochar samples were produced from pig manure by pyrolysis at different temperatures. One carbamate insecticide, carbaryl and one *S*-triazine herbicide, atrazine were selected as model pesticides. The adsorption and the catalytic hydrolysis of these two pesticides were studied on both original and deashed biochars. The mechanisms of adsorption and catalytic hydrolysis were then discussed.

2. Experimental

2.1. Materials

Carbaryl (98%) was obtained from Haili Chemical Company (Hunan, China), and atrazine (97%) was obtained from Rainbow Chemical Company (Shandong, China). The pesticides were used in batch experiments without purification. Analytical standards for the pesticides were purchased from Accustandard (Connecticut, US). Other chemicals used in this study were all analytical or HPLC grade.

2.2. Biochars

Pig manure stock was collected from a hoggery in Jixian County, Tianjin, China. The pig manure was air-dried and ground to pass through a 2-mm sieve. The manure was then heated at 350 °C or 700 °C in a ceramic pot covered with a tight-fitting lid (where oxygen was soon exhausted) in a preheated muffle furnace for 2 h [37]. The produced biochars were ground to pass through 0.038–0.075 mm (200–400 mesh) sieves and stored in amber glass bottles. Based on the temperature they were heated at, the biochars were designated as BC350 and BC700.

To remove the ash (deashing) of the biochars, the samples of the original biochars were treated with acid [38]. Batches consisting of 20 g of biochar were mixed and shaken in 200 mL of 1 M HCl for 10 h. That treatment was carried out 4 times for each batch. The entire procedure was then repeated using 200 mL of a 1 M:1 M HCl–HF solution. The treated biochars were rinsed with de-ionized water several times to remove residual acid and soluble salts until the solution pH was neutral. The resulting biochar samples were freeze-dried and stored in desiccators for later use. Base on the original heating temperatures, these deashed biochar samples were referred to as DABC350 and DABC700.

2.3. Characterization of biochars

Bulk organic elemental composition (C, H, and N) of the biochar samples was determined by an element analyzer (Elementar Vario EL, Germany). Ash content of the samples was measured by the residual weight after heating the biochars at 750 °C for 6 h [37], and the O content was calculated by mass difference. Surface elemental composition of biochars was quantified using an X-ray photoelectron spectrometer (XPS) (ULVAC-PHI PHI 5000 VersaProbe II, Japan). Surface area and pore volume were measured by a surface area analyzer (Quantachrome NOVA 2200e, USA). Solid-state ^{13}C NMR spectra were obtained by using the cross-polarization and total-sideband suppression (cptoss) method on a 7 mm magic angle-spinning (MAS) probe (BRUKER AVANCE III, Germany). Fourier transform infrared spectroscopy (FTIR) spectra of biochars were recorded between 4000 and 400 cm^{-1} wave numbers using an FTIR spectrometer (Perkin Elmer 1725 X, USA).

2.4. Batch sorption experiments

A total of four sorbents, i.e., BC350, BC700, DABC350, and DABC700, were studied. Sorption isotherms for each sorbent were determined at six different initial solution concentrations, with duplicate measurements at each concentration point. An aliquot of 50 mg of each sorbent was weighted into a 40 mL vial (US EPA) with a polytetrafluoroethylene (Teflon)-lined screw cap, followed by 40 mL of a background solution. The background solution contained 5 mM $CaCl_2$ to maintain a constant ionic strength and 200 mg/L $HgCl_2$ (pH 6.5) to inhibit aerobic biodegradation. After pre-equilibration for 24 h, designated amounts of pesticide stock solutions were spiked into each vial, with the volume percentage of methanol kept below 0.2% to minimize possible cosolvent effects on sorption. Initial concentrations of carbaryl were 1, 2.5, 5, 8, 20, 40 mg/L; while those of atrazine were 2, 4, 8, 10, 20, 30 mg/L. All of the vials were left with minimal head space and sealed with Teflon film. The vials were put in a shaker operated at 150 rpm and 20–24 °C in the dark for 24 h. The equilibration time was predetermined, and 24 h was confirmed to be enough to reach an apparent equilibrium. After equilibration, the vials were centrifuged at 3000 rpm for 20 min. Before analyzing by high performance liquid chromatography (HPLC), the supernatant was filtered through 0.45 μm PTFE syringe filters (Shanghai ANPLE, China), and external standards were also filtered to correct the solute loss due to filtration (less than 4%). The HPLC (Aglient 1200, USA) was equipped with a reverse phase column, Athena C18-WP (4.6 mm × 150 mm × 5 μm, 100 Å, CNW, Germany). The results of control samples without biochar indicated that the losses of pesticides by evaporation, photochemical decomposition, and sorption to vials, were less than 4%.

Details of pretreatment and analysis of samples were described in Supplementary Information (SI).