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# Sorption mechanisms of neonicotinoids on biochars and the impact of deashing treatments on biochar structure and neonicotinoids sorption<sup>☆</sup>

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## ABSTRACT

To elucidate the sorption affinity of biochars for neonicotinoid pesticides and the influence of biochar structure on sorption mechanisms therein, 24 biochar samples were obtained by pyrolyzing maize straw and pig manure at pyrolyzing temperatures (PTs) of 200–700 °C and by further deashing them using acids, and the sorption of three typical neonicotinoids, imidacloprid, clothianidin and thiacloprid on untreated and acid-deashed biochars were evaluated. All the biochar samples could efficiently adsorb the three neonicotinoids and multiple mechanisms were involved in sorption. With the increasing PTs, hydrophobic partition sorption increased, but had a declined contribution to the total sorption as revealed by a dual-mode model. Besides hydrophobic partition, specific interactions like cation- $\pi$  electron donor acceptor (EDA) interactions (only for protonated IMI and CLO) and hydrogen bond and contributed much to the sorption on low-PT ( $\leq 500$  °C) biochars, while the sorption on those high-PT ( $> 500$  °C) biochars mainly depended on pore-filling strengthened by cation- $\pi$  and  $p/\pi$ - $\pi$  EDA interactions. Thiacloprid showed stronger sorption on untreated biochars compared to imidacloprid and clothianidin, due to its greater ability to form hydrogen bond and hydrophobic interactions. Acid-deashing treatments increased the relative percentage contents of organic carbon, bulk O, aromaticity and O-containing functional groups, surface area and pore volume of biochars. The ash can bind neonicotinoids by specific interactions but played a negative role in the whole sorption on high-PT biochars by covering the inner sorption sites of organic moieties and blocking the micropores in biochars. The results acquired in the present study will help us to get deep insight in the comprehensive sorption mechanisms of polar pesticides on biochar and the effects of biochar structure.

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## 1. Introduction

Neonicotinoids were first developed and registered in the early 1990s, and have currently become the world's most widely used insecticides (Jeschke et al., 2011). Due to their great water solubility (Morrissey et al., 2015), neonicotinoids show high potential to leach into surface or underground waters, which is one of the major concerns about the extensive use of neonicotinoids in agricultural fields (Anderson et al., 2015; Botias et al., 2015; Huseth and Groves, 2014; Sadaria et al., 2016). In fact, neonicotinoids have been widely

detected in the environment with concentrations of parts per billion (ppb) -parts per million (ppm) in soil and parts per trillion (ppt) -ppb in water and ppb-ppm in plants (Bonmatin et al., 2015; Morrissey et al., 2015). In addition, adverse effects of neonicotinoids on non-target organisms like pollinators (Kessler et al., 2015; Rumke et al., 2015; Rundlof et al., 2015; Sadaria et al., 2016), insectivorous birds (Hallmann et al., 2014) and aquatic invertebrates (Morrissey et al., 2015) have also attracted extensive attention in recent years. The European Union issued a two-year's moratorium on some neonicotinoids in 2013, however, had to lift the ban due to the spread of pests (Rundlof et al., 2015). Hence, an effective method to reduce the mobility of neonicotinoids in agricultural fields is an alternative approach to reduce their adverse effects.

It has been well documented that biochars, derived by

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pyrolyzing biomass waste materials under anaerobic conditions, are a kind of promising sorbents for various chemical contaminants and biochar amendment to soils can enhance the sorption of certain pesticides (Cabrera et al., 2014; Delwiche et al., 2014; Loganathan et al., 2009; Lu et al., 2012; Spokas et al., 2014). It has been proved that biochars could behave as effectively as activated carbons in some cases but at a substantially lower cost (Alhashimi and Aktas, 2017). Multiple processes have been invoked to explain the sorption of pesticides on biochars. First, the high organic carbon (OC) content and great surface area (SA) of biochars provide plentiful sorption sites for pesticides (Beesley et al., 2011) via hydrophobic partition and pore-filling. Moreover, their great aromaticity, surface functional groups, and negative surface charge may strengthen the adsorption for pesticides via specific interactions, like  $p$  (lone pair electrons)/ $\pi$ - $\pi$  and cation- $\pi$  electron donor-acceptor (EDA) interactions, hydrogen bonds and electrostatic effects (Vijay and Sastry, 2010; Xiao and Pignatello, 2015a; Zhang et al., 2013). The structure and sorption capacity of biochar change greatly with raw materials and pyrolyzing conditions. Pyrolyzing temperature (PTs) is the most important factor in determining biochar structure and its sorption behavior. Usually, expansions of micro-porosity and increments in SA and aromaticity of OC happen with increasing pyrolysis peak temperature (Yavari et al., 2015). These changes in porosity and aromaticity make biochar more effective for immobilizing pesticides.

Besides organic matter and porosity, minerals can also sorb organic contaminants, however, its contribution to total sorption varies (Zheng et al., 2013). Usually, inorganic minerals reduce biochar sorption affinity for apolar organics, such as polycyclic aromatic hydrocarbons (Yang et al., 2011) by covering the micropores and sorption sites of organic moiety and lowering their accessibility (Wang et al., 2007). On the other hands, Li et al. (2017) reported that ash content removal decreased the sorption of bisphenol A on biochars acquired at 300–400 °C, due to the impact of mineral fraction in ash. These varied results indicate the lack of consensus in deashing effects on surface polarity of different materials as well as the sorption mechanisms of different sorbates. Therefore, further study is needed to elucidate deashing effects on the structure and physicochemical properties of biochars and their sorption affinity for polar neonicotinoids, and comparison between biochars obtained from different materials can provide important information since the amount and main components of mineral residues in biochar products depends greatly on those in the original biomass raw materials, e.g. plant residue vs. livestock manures.

Neonicotinoids are polar molecules with aromatic rings and plentiful polar groups, and some neonicotinoids exist as cations under natural pH. Hence, it can be predicted that multiple processes are involved in the sorption of neonicotinoids on biochars, which should be determined by the physicochemical properties of both biochar and neonicotinoid molecules. However, so far there are only several reports about the sorption of neonicotinoids on biochars, which only studied the effects of biochar amendment on soil adsorption of imidacloprid (IMI) and found that biochar addition enhanced the adsorption of IMI in soils (He et al., 2015; Jin et al., 2016). Hence, the capacity and mechanisms of neonicotinoids adsorption on different biochars are still unclear and need systematical study.

Hence, the objective of this study was to obtain deep insight into the sorption mechanisms of neonicotinoids on different types of biochars so as to find an effective biochar sorbent for neonicotinoids' sorption. To do so, a total of 24 biochar samples were acquired by pyrolyzing maize straw and pig manure at six different PTs and by further treating using HCl or HCl/HF on some of the original (untreated) biochars. The sorption of three typical neonicotinoids, IMI, clothianidin (CLO) and thiacloprid (THI), on these

biochars was systematically studied, and the effects of biochar structure and deashing treatment on the sorption mechanisms were investigated and discussed.

## 2. Materials and methods

### 2.1. Chemicals

Technical-grade imidacloprid (IMI, 98.5%), clothianidin (CLO, 98.5%) and thiacloprid (THI, 97.5%) were provided respectively by Ningbo Zhonghua Chemical Company (Zhejiang, China), Hebei-Veyong Bio-Chemical Company (Hebei, China) and Shandong Sino-Agri United Biotechnology Company (Shandong, China) without further purification. The molecular structures and selected physicochemical properties of the three neonicotinoids are listed in Table S1 in the Supplementary Information (SI). Other chemicals used in this study were all of HPLC or analytical grade.

### 2.2. Biochars

Maize straw and pig manure were collected from a farmland in Jiangsu province and a hoggery in Shandong province, China, respectively, and their properties are listed in Table S2. These materials were air-dried and ground to pass through a 2-mm sieve. Then, the dried materials were charred at 200, 300, 400, 500, 600, 700 °C for 4 h in a crucible with a cover under oxygen-limited conditions in a muffle furnace (Tianjin Zhonghuan Company, China). The produced biochars were ground to pass through 40–200 mesh (0.075–0.425 mm) sieves and stored in 500-mL amber glass bottles in 200-L desiccators. The biochars are referred as untreated biochars compared to those acid-treated biochars (deashed biochars). Based on the raw materials and the PTs, the biochars are designated as MBCn00 (maize straw) and PBCn00 (pig manure), with n00 indicating PTs (200–700 °C), and when the raw materials are not distinguished, the biochars are designated as BCn00 or untreated biochar as a whole with the same PT.

To remove the ash from biochars, the untreated biochars obtained at 300, 500 and 700 °C were treated with acids. Suspensions containing 20 g of untreated biochar and 200 mL of 1 M HCl were shaken for 10 h in the dark. The process was repeated 4 times for each batch to obtain lightly-deashed biochars (LD-M(P)BCn00). The deeply-deashed biochars (DD-M(P)BCn00) were obtained by further treating the LD-BCs using 200 mL of a 1 M: 1 M HCl-HF solution for 10 h. After the reaction, the acids were replaced by deionized water to rinse the acid-treated biochars, which were repeated 6–8 times to remove the acids as well as soluble salts until the solution pH reached to 6.5–7.0. The acid-deashed biochars were freeze-dried and stored in 500-mL amber glass bottles in 200-L desiccators until late use. A total of 24 biochar samples were acquired (Table S3).

Bulk elemental composition, i.e. the relative mass percentages of C, H, and N of the total mass of biochar samples were measured by an Elementar Vario EL element analyzer (Germany). Ash content was determined by the residual weight after sufficient burning of biochars at 750 °C for 6 h (Keiluweit et al., 2010), and the mass difference between total mass and C, H, N and ash contents was used to calculate the relative percentage content of O. Biochar surface elemental composition was quantified using an ULVAC-PHI PHI 5000 Versa Probe II X-ray photoelectron spectrometer (Japan). Pore volume and SA were determined by a Quantachrome NOVA 2200e SA analyzer (USA). Distribution of functional groups were acquired based on solid-state  $^{13}\text{C}$  NMR spectra obtained using a BRUKER AVANCE III solid-state  $^{13}\text{C}$  NMR (Germany) with a cross-polarization and total-sideband suppression method on a 7 mm

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