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Variation in sorption of propiconazole with biochars: The effect of temperature, mineral, molecular structure, and nano-porosity

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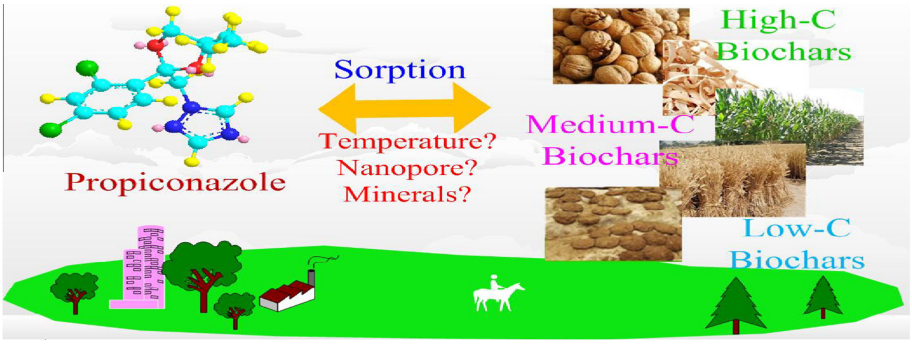
HIGHLIGHTS

- Surface polar groups mainly consisted of O-containing groups of minerals.
- Pore-filling in aromatic C of biochar control nonlinear propiconazole sorption.
- HTT or C contents of biochar didn't necessarily control propiconazole sorption.
- Minerals may exert certain influence on propiconazole sorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Sorption behavior of propiconazole (PROPI) by plant-residue derived biochars (PLABs) and animal waste-derived biochars (ANIBs) obtained at three heating treatment temperatures (HTTs) (300, 450 and 600 °C) (e.g., BCs300, BCs450, and BCs600) and their corresponding de-ashed BCs450 was investigated. PLABs belonged to high- or medium-C biochars and ANIBs were low-C biochars. Surface C concentrations of the tested biochars were generally higher than their corresponding bulk C. Surface polar groups were mainly composed of O-containing groups of minerals within biochars. The nonlinearity coefficients (*n*) of propiconazole (PROPI) sorption isotherms ranged from 0.23 to 0.64, which was significantly and negatively related to organic carbon (OC)–normalized CO_2-surface area (CO_2-SA/OC) of biochars. This correlation along with the positive relationship between CO_2-SA/OC and aromaticity indicates that pore-filling in nanopores within aromatic C dominate nonlinear PROPI sorption. HTTs or C contents do not necessarily regulate PROPI sorption. Removal of minerals from BCs450 elevated PROPI sorption because minerals may exert certain influence on sorption via impacting spatial arrangement of polar groups and/or organic matter (OM)–mineral interactions. This study helps to better understand sorption behavior of PROPI to biochars and evaluate the potential role of biochar in water treatment systems.

1. Introduction

Pesticide use in agriculture has been instrumental in increasing crop yields and efficiency in the food production processes supplying food to an ever-increasing world population. However, the use

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of pesticides has led to a series of toxicological and environmental risks, which has drawn extensive attention from all aspects of society (Li and Randak, 2009). Innovative strategies are needed to reduce the environmental impact of pesticides, while improving agricultural productivity. Biochar is a porous carbon rich charcoal-like substance created by heating waste biomass under low oxygen conditions or anaerobic conditions. Biochar has been used as an increasingly utilized cost-effective soil amendment in agricultural and environmental applications (Sohi et al., 2010; Beesley et al., 2011), which can reduce greenhouse gas emissions, sequester C, as well as improve soil fertility and thus plant growth (Steinbeiss et al., 2009; Atkinson et al., 2010; Woolf et al., 2010). Moreover, biochar has a large surface area and high microporosity, which results in a very high affinity and capacity for sorbing and immobilizing organic contaminants (Keiluweit et al., 2010; Kookana, 2010; Sun et al., 2011a, 2011b). To date, there has been a growing body of literature on the application of biochar in water treatment reviewed by Inyang and Dickenson (2015). In particular, the use of biochar for the removal of persistent organic pollutants from aqueous systems has been addressed (Liu et al., 2012; Zheng et al., 2013; Chen et al., 2015). The sorption behavior of some pesticides and herbicides as well as their removal mechanisms has been previously documented. For an instance, the removal performance of atrazine (Cao et al., 2009), catechol (Kasozi et al., 2010), carbaryl (Zhang et al., 2013), 2,4-Dichlorophenoxyacetic acid (Kearns et al., 2014), fluridone (Sun et al., 2011a), and oxamyl (Taha et al., 2014) by various biochars was 0.02, 20, 1, 0.72, 10 mg g^{-1}, and ~99% sorbed, respectively, and their removal mechanisms (e.g., proposed sorption mechanisms) were mainly partitioning, pore-filling and diffusion, hydrophobic and π–π EDA interaction, surface adsorption, partitioning on armorphous-C, and H-bonding with polar groups, respectively. However, knowledge on the sorption propiconazole (PROPI) by biochar is very limited. PROPI is a hydrophobic systemic triazole fungicide, which is used worldwide for controlling harmful microorganisms, inhibiting fungus attack and preventing foliar or root disease, such as powdery mildew, leaf spot, rust and root rot (Garland et al., 1999). PROPI has been listed as a persistent, potentially toxic compound and possible human carcinogen by the European Union (Adam et al., 2005). Its low mobility and relatively high adsorption in soils rich in OM result in its accumulation in soils and pose a risk for the soil ecosystem (Thorstensen et al., 2001). Organic carbon (OC) has been reported to be the most important factor in adsorption of PROPI by soils (Riise et al., 2001). Therefore, it is hypothesized that rich-OC biochar should have high sorption capacity to PROPI and there is practical application of biochar in water treatment containing PROPI.

The ability of biochars to sorb organic pollutants depends greatly on their physical and chemical properties, which vary dramatically with heating treatment temperatures (HTT) and feedstock sources (Chen et al., 2008; Sun et al., 2012). Recently, Keiluweit et al. (2010) proposed a multiphase model to describe the physical–chemical transitions in char as HTT is increased. They found four distinct categories in biochars derived from grass and wood residues: transition char, amorphous char, composite char, and turbostatic char, which exhibited different molecular structure as well as surface characteristics. Their differences in these properties influenced their sorption properties of phthalic acid esters (PAEs) and fluorinated herbicides, moreover, the grass biochars generally exhibited higher sorption to PAEs and herbicides than the wood biochar from the same temperature (Sun et al., 2011a, 2012). On the other hand, previous studies on the sorption of hydrophobic organic contaminants (HOCs) generally used low-mineral biochars produced from relatively pure plant residues (Smernik, 2009). Although some of these contain considerable ash (e.g. grass biochars), the sorption properties of the ash component have been little considered (Smernik, 2009; Sun et al., 2012). For sorption of HOCs, it is reasonable to assume that the OM still would dominate the sorption of mineral-rich biochars, however, the presence of minerals is likely to have at least a secondary influence (Smernik, 2009). Information about effects of minerals on the sorption of biochars to pesticides, as well as the related OM-mineral interaction mechanism, is rather limited to date. In addition, earlier studies dealt with the role of bulk polarity of biochars on their sorption of HOCs (Chen et al., 2008; Sun et al., 2012), while the impact of their surface polarity on pesticides sorption was seldom investigated, especially for PROPI. It was hypothesized minerals and components (e.g., aromaticity, ash content, bulk or surface polarity) within biochars (exogenous OM of soils) should influence sorption of PROPI.

This study was designed to fill this knowledge gap. Twelve feedstocks from plant residues and animal-wastes that contained various contents of ash were used to produce biochars at three HTTs (300, 450, 600 °C). In addition, the six selected biochars were de-ashed to investigate the influence of the minerals on sorption of PROPI. The primary objectives of this study were to: (1) investigate the effect of both HTT and feedstock on the biochar characteristics and, in turn, their effect on the sorption behavior of PROPI; (2) gain insight into the principal factors or components (e.g., aromaticity, ash content, bulk or surface polarity) controlling sorption of PROPI by each kind of biochar; and (3) identify the impacts of minerals on the sorption of PROPI by biochars.

2. Materials and methods

2.1. Chemicals

PROPI (with a purity > 98%) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The molecular structure and selected physicochemical characteristics of PROPI are presented in Table S1, Supplementary data. A stock solution of 100,000 mg/L of PROPI was prepared in methanol and stored at 4 °C in the dark.

2.2. Sorbents

Biochars were produced from two types of feedstocks (9 plant residues: walnut shell, pine wood, poplar leaf, cotton straw, bean straw, potato straw, rice straw, wheat straw, maize straw; and 3 animal wastes: manure of chicken, swine, and cow) at three different HTTs to obtain 27 plant-derived biochars (PLABs) and 9 animal waste-derived biochars (ANIBs). In addition, six biochars produced at 450 °C were also de-ashed. Detailed descriptions of the production procedures of biochars as well as their de-ashed samples can be found in Sun et al., 2013a; Jin et al., 2014; Qiu et al., 2014. The biochar samples are referred to as WALX, PINX, POPX, COTX, BEAX, POTX, RICX, WHEX, MAIX, CHIX, SWIX, and COWX, according to the first three capital letters of source material name, where X is substituted with the appropriate HTT (300, 450 and 600 °C). For comparison, fresh raw material ($X = 000$) was also included in some analyses. A “D” preceding the sample name is used to identify the de-ashed counterparts. The groups of biochars produced at 300, 450 and 600 °C are also referred to as BCs300, BCs450, and BCs600, respectively. Some of the biochars in this study have been used in previous studies in order to investigate (a) the impact of deashing treatment on biochar structure properties and potential sorption mechanisms of phenanthrene by six biochars from plant residues (rice, wheat, maize), and animal waste (chicken, swine, cow) at 450 and 600 °C (Sun et al., 2013a, (b) the competitive sorption of phenanthrene and dibutyl phathalate by five BCs450 produced from grass straws (soybean, rice, and cotton), pine wood dust and swine manure (Jin et al., 2014); and (c) properties of PLABs and ANIBs produced at 300 and 450 °C as well as their sorption properties of dibutyl phthalate (Qiu et al., 2014).

2.3. Characterization of biochars

The bulk elemental (C, H, N, O) properties of biochars were obtained using an Elementar Vario ELIII elemental analyzer. The elemental C composition value (wt%) is also referred to as the C content or OC content (Sun et al., 2013a). The ash content was calculated by heating biochars at 750 °C for 4 h. The H/C and $(O+N)/C$ atomic ratios are used to evaluate the aromaticity and polarity of the biochars. Pore size distribution (PSD) and cumulative surface area (SA) up to 1.4 nm (micropores) were determined from CO_2 (CO_2-SA) isotherms at 273 K using an Autosorb-1 gas analyzer (Quantachrome Instrument Corp., Boynton Beach, FL) with CO_2 isotherm at 273 K. CO_2-SA was calculated using nonlocal density functional theory (NLDFT) and grand canonical Monte Carlo simulation (GCMC) (Sun et al., 2013a; Jin et al., 2014). Nitrogen gas (N_2) adsorption was performed at 77 K using an Autosorb-iQ gas analyzer (Quantachrome Instrument Corp., Boynton Beach, FL). The N_2-SA was calculated from the Brunur-Emmett-Teller method applied in the region of relative pressures from 0.05 to 0.3 of P/P_0. Solid-state cross-polarization (CP) and magic angle spinning (MAS) ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra of original biochars were obtained by using a Bruker Avance 300 NMR spectrometer (Karlsruhe, Germany) for information on chemical composition. The NMR running parameters and chemical shift assignments are described in Supplementary data. Surface elemental composition was examined using X-ray photoelectron spectroscopy (XPS) with a Kratos Axis Ultra electron spectrometer using monochromated Al Kα source operated at 225 W. A more detailed account of the characterization procedures of NMR and XPS as well as the chemical shift assignments of NMR is available in our previous study (Sun et al., 2013a).

2.4. Sorption experiments

A batch equilibration was conducted in 15 mL glass centrifuge tubes. Preliminary experiments showed that loss of PROPI was less than 1% during the whole experimental process, implying the sorption on tested tubes and photodegradation of PROPI were negligible. Appropriate amounts of sorbents were used to ensure that 20–80% uptake of initially added PROPI was obtained. The stock solution was diluted sequentially to a series of initial concentrations (100–100,000 μg/L) using background solutions (containing 200 mg/L NaN_3 to minimize bio-degradation, and 0.01 M $CaCl_2$ to maintain a constant ionic strength). The volume ratio of methanol to water was controlled below 0.001 to avoid cosolvent effect. Preliminary tests and kinetic experiment showed that the apparent sorption equilibrium was reached before 10 d according the kinetics of PROPI sorption by the selected six biochars (Fig. S1, Supplementary data). All vials were sealed with Teflon screw caps and shaken for 10 d at room temperature (25 °C). After mixing, all the vials were centrifuged for 15 min at 1000 rpm, and 2 mL of each supernatant was transferred and analyzed employing high-performance liquid chromatography (HPLC) (1260 Series, Agilent Technologies, Santa Clara, CA) to get solution-phase sorbate concentration. The HPLC was equipped with a reversed-phase C18 analytical column (5 μm, 4.6 mm × 250 mm) and a UV detector. The mobile phase consisted of 80% methanol and 20% water at a flow rate of 1 mL/min. The detection wavelength of a UV detector was set at 205 nm. The injection volume was 10 μL, and temperature of the column was 30 °C. The PROPI was eluted from the column at 5.0 min. The concentrations of PROPI in the standard curve, which was used to measure original (C_0) and equilibrated concentrations (C_e) in solutions, ranged from 20 μg/L to 100,000 μg/L. All the experiments including the blanks were run in duplicate and performed at room temperature (25 °C) in the dark. The mass of adsorbed PROPI was calculated by mass difference between C_0 and C_e. Control experiments were run in the same concentration sequence of PROPI solution without sorbents. The concentrations of PROPI within the background solutions before and after addition of biochar were the same. The limit of detection was 20 μg/L.

2.5. Data fitting

The Freundlich model (FM) was employed to fit the equilibrium sorption data of PROPI by biochars.

Freundlich model:

$$\log q_e = \log K_f + n \log C_e \quad (1)$$

where q_e (μg/g) is the sorbate concentration in the solid phase, C_e (μg/L) is the equilibrium concentration of the liquid phase, n is the isotherm nonlinearity index, K_f [(μg/g)/(μg/L)^n] is the affinity coefficient of Freundlich model.

The sorption distribution coefficient (K_d) and the OC-normalized K_d (K_{oc}) were obtained by the Eq. (2) and (3).

$$K_d = q_e/C_e \quad (2)$$

$$K_{oc} = K_d/f_{oc} \quad (3)$$

where f_{oc} is OC content (%), $C_e = 0.01\ C_s$, and C_s is the water solubility of PROPI. The K_d and K_{oc} values of original and de-ashed biochars were calculated according the above equations. The investigated correlations among properties of sorbents as well as their sorption coefficients of PROPI (Pearson correlation coefficients: P and R values) were obtained from the Pearson correlation analysis by SPSS 16.0 software (SPSS Inc., USA).

3. Results and discussion

3.1. Characterization of the biochars

Three categories for the classification of biochars according to their carbon content have been proposed—high (>80%), medium (60–80%), and low (<60%) (Joseph et al., 2009). Two PLABs biochars produced at 600 °C had a high C content: WAL600 and PIN600 exceeded 80% (Fig. 1, Table S2, Supplementary data), which is consistent with reports that biochars from wood residue at high temperatures (>500 °C) generally belong to high-C biochars (Joseph et al., 2009). The other PLABs produced at 600 °C belonged to the medium-C biochar, their C content varied from 60% to 80%, while the ANIBs obtained at 600 °C were in the third category (e.g., low-C biochars) due to the high abundance of ash (52.3–89.0%) (Table S2, Supplementary data). The ash content of all the biochars varied greatly and ranged from 2.0% to 89.0% (Table S2, Supplementary data). This classification of biochars provides a measure for the total amount of OC that is added to the soil via char addition and is therefore necessary to determine the C balance and sequestration potential of biochar management. It is also a good indicator of the composition of the parent biomass and the process conditions under which the biochar is produced (Joseph et al., 2009). Further analysis of the elemental concentrations of C, H, and O via a plot of the relationship between the H/C and O/C molar ratios (i.e., a van Krevelen diagram) shows the effect of the pyrolysis conditions on the chars. In general, both molar ratios in the studied biochars decreased with increasing HTTs (Fig. S2, Supplementary data). The progressive decrease in H/C ratio is

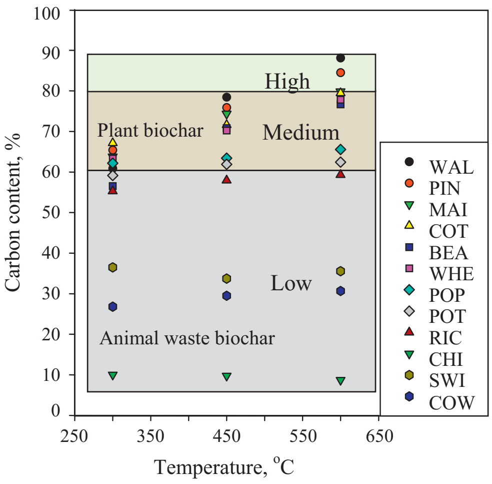

Fig. 1. Classification of biochars as high, medium and low C-containing as a function of temperature for different feedstocks: production of biochars from plant residues (walnut: WAL; pine wood: PIN; maize straw: MAI; cotton straw: COT; bean straw: BEA; wheat straw: WHE; poplar leaf: POP; potato straw: POT; rice straw: RIC) and from animal and poultry waste (chicken manure: CHI; swine waste: SWI; cow manure: COW).

indicative of the formation of structures containing unsaturated carbons such as aromatic rings. All samples of raw materials (BCs000) fall within the compositional space for pure carbohydrate and lignin (Fig. S2, Supplementary data). The biochars showed a progression towards graphitic like materials with increasing HTTs. The principal change in the elemental composition of the thermally altered residue was due mainly to dehydration.

Characterization of the surface compositions of the thirty-six biochars and six their selected de-ashed biochars was carried out with XPS (Table S2, Supplementary data). The surface C concentrations of the biochars were generally higher than their corresponding bulk C (Fig. 2a). The difference between the two C contents (surface and bulk) correlated positively with their ash content (Fig. 2b and Table S2, Supplementary data), indicating that C concentrates on the surface of the biochar particles. The bulk polarity index ((O + N)/C) of all biochars diminished with increasing HTTs, while less difference was found in the surface polarity index for these biochars (Fig. 2c and d), suggesting that the O-containing polar groups of the minerals within biochars were likely the major contributor to their surface polarity. The bulk polarity of BCs300 (except COW300 and CHI300) was generally higher than their surface polarity, while the opposite trend was found for the BCs600 especially for high-mineral biochar (Table S2, Supplementary data). The surface polarity of biochars was positively related to their ash contents especially at higher HTTs (Fig. 2e), showing that the minerals greatly influence the surface polarity of biochars. Moreover, the de-ashing treatment of the biochars with high ash content reduced the surface polarity to a large extent. The N content of the feedstock varied considerably, ranging from 0.09% of the pine wood to 3.66% of the poplar leaf. Comparison of the N content of the surface and bulk composition relative to the C content (Fig. S3) showed that during the pyrolysis process there is a trend towards an enrichment of N-containing compounds at the surface, except for POP and SWI.

The N_2 and CO_2 adsorption techniques were used to characterize the heterogeneity of surfaces and porosity of biochars and to obtain information about the distribution of OC within biochar aggregates (Table S2, Supplementary data). N_2 is adsorbed primarily on the outer surface of soil particles. Pignatello et al. (2006) reported that N_2 may not detect black carbon (BC) microporosity in geosorbents within reasonable equilibration times and at 77 K. Therefore, CO_2 adsorption at 273 K has been proposed as an alternative to characterize nano-porosity in soils, because CO_2 at 273 *K* can enter the micropores (0–1.4 nm) (Sun et al., 2013a). The values of N_2-SA for all BC300s and BC450s were low, most well below 7 m^2/g. On the contrary, a dramatic elevation in N_2-SA was observed for BC600 samples with values from 35 to 285 m^2/g, excepting POP600, COW600, and CHI600 (Table S2, Supplementary data). Lattao et al. (2014) also reported that N_2-SA of the chars derived from maple wood at 300, 350, and 400 °C is <10 m^2/g, rising sharply to a maximum of 332 m^2/g for the char produced at 500 °C. A positive and significant relationship between bulk C content and N_2-SA of BC600 samples excluding POP600, along with the negative and significant correlation of N_2-SA of BC600 samples to their ash contents suggests that the high N_2-SA values of BC600 samples are due to the OC of biochars instead of their minerals. Indeed, the de-ashed samples of COW450 and CHI450 show much higher values than those at both 450 °C and 600 °C. These results are consistent with XPS findings in this study that the surface C was generally higher than the corresponding bulk C content.

The CO_2-SA of biochars also went up with increasing HTT, however, some micropores already existed in the lower temperature biochars as indicated by their relatively high CO_2-SA compared to their N_2-SA. It has been postulated that CO_2 has a high affinity for OC and, possibly, microporous regions of soils (Ravikovitch et al., 2005). The positive and significant correlation of CO_2-SA to the bulk C content (Fig. 2f) supports this conclusion.

The results of the PSD profiles estimated from the CO_2 isotherm at 273 K for biochars from 7 feedstocks corroborate that most of biochars, excluding CHI biochars, were highly microporous (Fig. S4, Supplementary data). Nearly all porosity lies in pores with diameters 1.4 nm or less, which is consistent with the pore size of char reported by Kwon and Pignatello (2005) and Lattao et al. (2014). Pores of 0.4–0.6 nm and less than 1 nm accounted for 50–75% and 86–92%, respectively, of cumulative pore volume from 0 to 1.4 nm and the percentages varied with different feedstock and HTT of biochars (Fig. S4 and Table S3, Supplementary data).

In order to investigate where (aromatic or aliphatic C) micropores of OC within biochars exist, the relationships between CO_2-SA normalized by OC content (CO_2-SA/OC) and the contents of functional groups detected by ^{13}C NMR (Table S4, Fig. S5, Supplementary data) were analyzed. The CO_2-SA/OC values of biochars excluding WAL300 were significantly and positively correlated with aryl C content (or aromaticity) (%) (Fig. 2g), simultaneously, significant and negative relationships between CO_2-SA/OC values of biochars and the content of aliphatic C or polar C (45–93 ppm) were also observed (Fig. 2h), which suggests that the nanopores of OC are located in the aromatic moieties associated with the tested biochars.

3.2. Sorption isotherm of propiconazole

The Freundlich isotherms are presented in Fig. S6 and the fitting parameters are listed in Table S5, Supplementary data. The nonlinearity index *n* values ranged from 0.23 to 0.64, suggesting that the sorption isotherms of PROPI by the tested biochars were remarkably nonlinear, since the *n* values are much less than 1. The *n* values of sorption isotherms of PROPI were correlated to the properties of the test biochars to investigate which factors influence the nonlinearity of the PROPI sorption. The significant and positive relationships between *n* and the percentage of alkyl-C (Fig. 3a), the O content (Fig. 3b), the polarity index ((O + N)/C) (Fig. 3c), and the percentage of polar C obtained from the ^{13}C NMR results (Fig. 3d) were observed, suggesting that the alkyl-C and polar groups (except the O-aryl groups) of the tested biochars are responsible for the linear partition of PROPI. On the other hand,

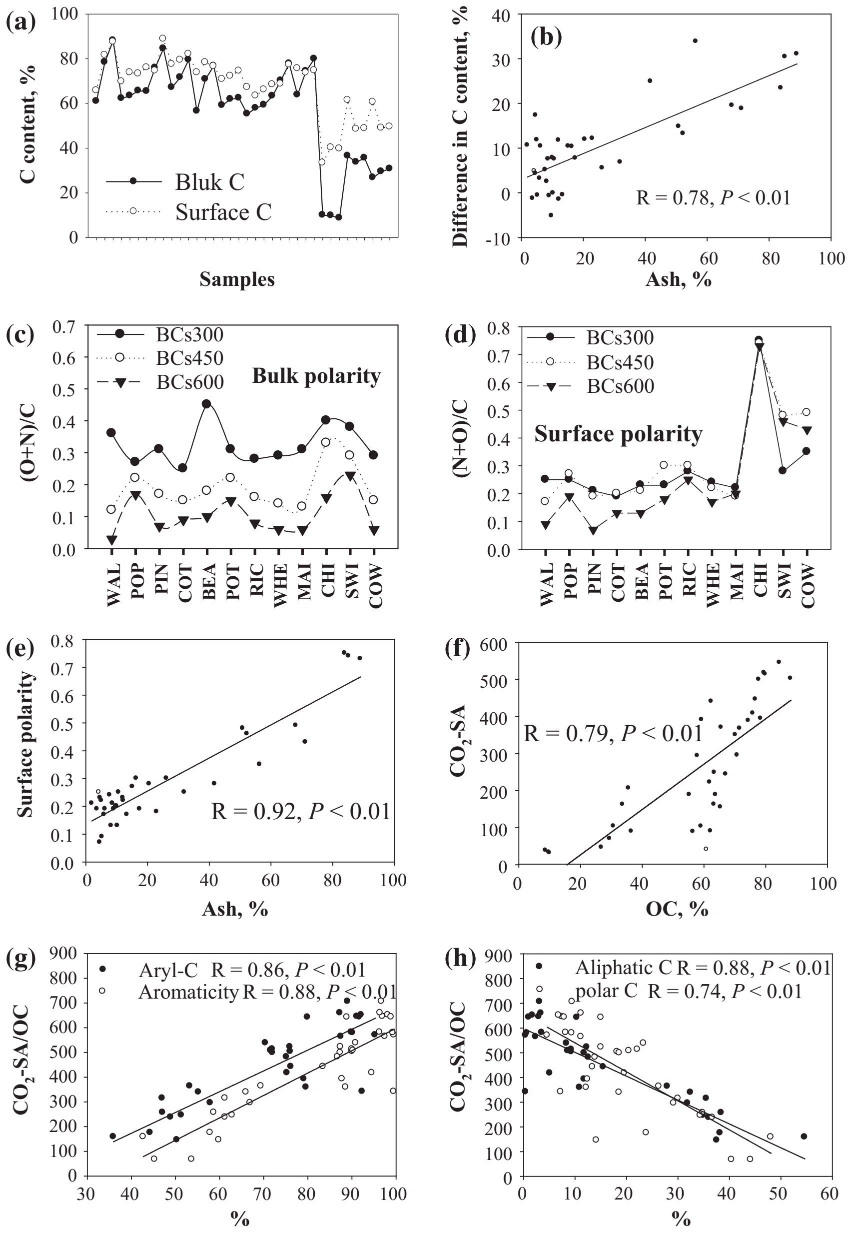

Fig. 2. Comparison of C between the bulk and surface contents of biochars (a); correlation between the difference in bulk and surface C contents and ash content of biochars (b), comparison of bulk polarity ((O + N)/C) according to bulk elemental composition (c) and surface polarity((O + N)/C) as indicated by surface elemental composition (d) among these biochars produced at 300, 450, 600 °C (e.g., BCs300, BCs450, and BCs600); relationships between surface polarity and the ash contents of biochars (e), between organic carbon (OC) and CO_2 surface area (CO_2-SA) (f), between aryl-C content or aromaticity and OC-normalized CO_2-SA (CO_2-SA/OC) (g), and between aliphatic C content or polar C content and CO_2-SA/OC (h).

the *n* values of sorption isotherms of PROPI were significantly and negatively related to aromaticity (Fig. 3e), which implies that the aromatic C of the biochars is responsible for the nonlinear sorption of PROPI. The significant and positive correlation of the *n* values to the atomic ratio of *H*/*C* (Fig. 3f) also supports this conclusion. Therefore, the elevated nonlinearity of sorption isotherm of PROPI with the increasing HTTs (Fig. 3g and Table S5, Supplementary data) could be attributed to the rising aromaticity and decreasing *H*/*C* of biochars with the increasing HTTs (Tables S2 and S4, Supplementary data) (Chen et al., 2008). In investigating the sorption behavior of the two herbicides, norflurazon and fluridone, to biochars produced from wood and grass feedstocks, Sun et al. (2011a) observed the onlinearity of their sorption isotherm enhanced with the increasing HTTs as this study. Pignatello and Xing (1996) reported that microporosity gives rise to isotherm nonlinearity, which is indicative of a distribution of site energies. Using SA-CO_2/OC as a measure of the microporosity of the biochars, it can be seen that there is a significant and negative relationship between microporosity and the nonlinearity index *n* values of PROPI (Fig. 3h). This relationship along with the positive and significant correlation of SA-CO_2/OC of the biochars to their aromaticity (Fig. 2g) suggests the pore-filling resulted by the nanopores from aromatic C dominate the nonlinear sorption of PROPI by biochars. This finding supports the conclusion that aromatic carbon within engineered carbonaceous geosorbents regulates the nonlinear adsorption of HOCs (Han et al., 2014). Therefore, this result could help shed light on the ongoing debate about the importance of aromatic and aliphatic carbon components of carbonaceous geosorbents in governing the sorption of HOCs; that is, the sources of carbonanceous georbents (e.g., the natural OM

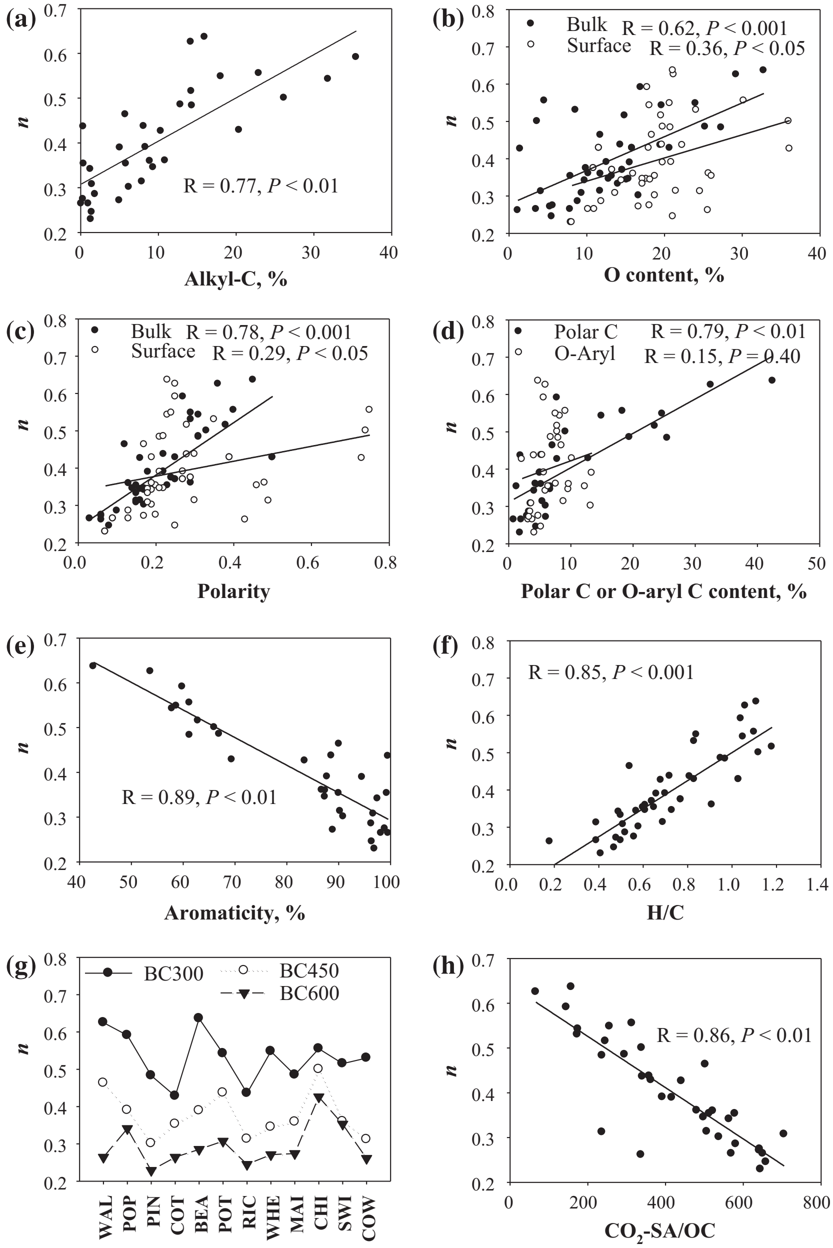

Fig. 3. Relationships between nonlinear sorption coefficients (n) of propiconazole by biochars and their alkyl-C content (a), bulk or surface O contents (b), bulk or surface polarity ((N + O)/C) (c), polar C or O-aryl C contents (d), aromaticity (e), the atomic ratio H/C (f), and organic carbon (OC) normalized CO_2 surface area (CO_2-SA/OC) (h); comparison of n values among these biochars produced at 300, 450, 600 °C (e.g., BCs300, BCs450, and BCs600) (g). (Polar C: 45–93 ppm + 165–220 ppm; O-aryl C: 148–165 ppm; Aromaticity = 100 × aromatic C (93–165 ppm)/[aromatic C (93–165 ppm) + aliphatic C (0–93 ppm)]).

(NOM) or the engineered OM) should be considered during investigating the importance of aromatic and aliphatic carbon of geosorbents in governing the sorption of HOCs. Recently, Sun et al. (2013b) found that adsorption volumes of both benzene and phenanthrene by NOM are significantly related to the aliphatic C content, and their correlation lines are nearly overlapped, suggesting that the nanopore filling is the dominating mechanism for the sorption of phenanthrene and benzene by the NOM samples and also sorption is not affected by water molecules (Cornelissen et al., 2005; Sun et al., 2013b). Thus, the nanopores within the aliphatic moieties of their investigated NOM samples might play an important role in the adsorption of HOCs. However, soils and sediments, respectively, generally contain BC materials, making up 4% and 9% of total organic carbon (TOC) (Cornelissen et al., 2005), which behave differently than the other NOM. BC materials, including purified char or char from soils and sediments, have high surface areas and porosity within their aromatic components, facilitating strong and nonlinear adsorption of HOCs (Cornelissen and Gustafsson, 2004; Cornelissen et al., 2005; Koelmans et al., 2006). If soils or sediments are not contaminated by BC materials, it can be expected that the role of the aliphatic components in the sorption of HOCs should be dominant. It is likely that BC materials frequently hinder scientists in uncovering the sorption mechanism of HOCs by NOM due to their ubiquitous occurrence in soils and sediments.

The K_d of PROPI for all biochars along with the related K_{oc} are shown in Table S5, Supplementary data. Neither of the distribution coefficients for the 36 biochars exhibited clear trends with the HTTs in this study (Table S5, Supplementary data), indicating that HTTs of the biochars do not necessarily dominate the sorption behavior of PROPI. In contrast, previous studies with biochars from only one or two feedstocks reported that chars produced at lower temperatures had greater sorption capacity for polar organic contaminants than those made at higher temperatures (Sun et al., 2011a. 2012; Lü et al., 2012, 2012; Chen et al., 2008). This difference may be due to the limited variation in chemical compositions (e.g., aromaticity or polar functional groups) as well as conformation of the biochars in those studies. In order to investigate the influence of such biochar properties on the sorption capacity of PROPI, the sorption parameters (K_d and K_{oc}) were correlated to additional properties of the two groups of biochars. Besides the significant and negative correlation of surface Si content of the ANIBS to the K_d values of PROPI (Fig. S7a, Supplementary data), the ash content of the ANIBs was observed to be negatively related to their K_d values while the inverse trend was found for the PLABs (Fig. S7b and c, Supplementary data), indicating that the minerals of ANIBs and PLABs have the different effect on their PROPI sorption. The minerals associated with the PLABs encourage the PROPI sorption, while the minerals of the ANIBs play the opposite role. For the PLABs, there was no relationship between their OC content or polarity and the K_d values of PROPI (not shown), suggesting that these were not dominant factors in regulating the sorption of PROPI on PLABs, possibly due to their chemical and physical heterogeneity (e.g., composition and conformation) resulting from their complicated feedstocks. In contrast, the OC content of the ANIBs dominated their sorption of PROPI (Fig. S7d, Supplementary data). The K_d values of ANIBs are positively related to the bulk O content associated with OM of the ANIBs and negatively to surface O of the ANIBs (Fig. S7e and f, Supplementary data), suggesting that the polar groups associated with OM within the ANIBs facilitate the sorption of PROPI, while the polar groups of minerals likely block the PROPI from entering the sorption sites of OM within the ANIBs, thus reducing its sorption by the ANIBs. The K_d values of all tested biochars generally enhanced with the increasing content of aryl-C (Fig. S7 g, Supplementary data), implying that aryl-C of the biochars should be mainly responsible for their sorption of PROPI.

3.3. Effect of de-ashing treatment on nonlinearity n values and sorption capacity K_{oc} of three kinds of biochars

To study the influence of the minerals in the biochars on the sorption of PROPI, the sorption capacity index (K_{oc}) and nonlinearity index *n* were measured for six de-ashed biochars produced at 450 °C (Table S5, Supplementary data). De-ashing treatment did not have a large impact on the nonlinearity index (Table S5, Supplementary data); this contrasts with a previous report that the removal of mineral components may create additional accessible sorption sites on BC, thus giving rise to a more heterogeneous distribution of sorption sites, and enhancing nonlinear adsorption (Ji et al., 2011). The inconsistent results may be attributable to the difference in polarity between their solutes (higher polar tetracycline and sulfamethoxazole) and PROPI. The nonlinearity *n* values of PROPI sorption were observed to be related to C-functional groups, bulk O and polarity, and H/C of the tested biochars (Fig. 3). While de-ashing treatment had no remarkable influence on C-functional groups, bulk O and polarity for most of the BCs450 except for the bulk O and polarity of CHI450 (Table S2, Supplementary data), therefore, its nonlinearity of PROPI was enhanced (Table S5, Supplementary data) due to the aforementioned positive correlations.

It was observed that the K_{oc} values of PROPI ($C_e = 0.01C_s$) by biochars increased after de-ashing treatment, especially for the ANIBs, and their log K_{oc} values increased from 3.10–3.69 to 3.32–4.14 (Table S5, Supplementary data), suggesting the removal of the minerals elevate the PROPI sorption of the biochars. Moreover, another evidence for the importance of minerals was confirmed by the positive correlation between the ash content of original BCs450 and their increased K_d values of PROPI after removal of minerals (Pearson correlation coefficient $R = 0.96$, $P < 0.01$) (Fig. S7 h, Supplementary data). The de-ashing treatment removed most of the mineral components (mainly silicates), which prevent sorbate's access to the sorption sites within sorbents, thus the removal of minerals enables biochars to possess more available hydrophobic sorption domains and less polar functional groups (Bonin and Simpson, 2007; Ahangar et al., 2008; Ji et al., 2011), enhancing accessibility of PROPI to the hydrophobic organic carbons in biochars. Therefore, minerals play an important role in regulating the accessibility and distribution of sorption sites for pesticides.

4. Conclusions

This study investigated the influence of both HTTs and minerals on the molecular structure of bulk and surface OC, the bulk and surface polar groups (e.g., polarity), and microporosities in the biochars. The distribution of OC and polar groups associated with both OM and minerals within the tested low-, medium- and high- C biochars, which became very important to better understand the properties of different kinds of biochars. The sorption isotherms of PROPI by biochars were nonlinear and nanopores within aromatic C of these biochars were responsible for the nonlinear sorption of PROPI. The minerals of ANIBs and PLABs had opposite effect on the sorption coefficient (K_d). De-ashing treatment altered the physicochemical properties of biochars through the removal of most minerals, which in turn affected their sorption of PROPI. These data help us better understand sorption mechanisms of PROPI by organic matter–mineral complexes in biochars, and could be useful for assessing the potential of applying biochar in water treatment operations to remove pesticides. However, because each kind of biochar has particular sorption properties for a pesticide as a result of different feedstocks and production parameters (De Pasquale et al., 2012; Sun et al., 2012), its suitability for surrogatees of activated carbons cannot be generalized, so more research is needed to investigate the effects of biochars on removal performance of pesticide.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.07.018.

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