# The characteristics of different derived biochars and their sorption behavior for Diethyl phthalate (DEP)

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**Abstract.** The characterization of two categories by plant residue and animal waste derived biochars obtained at 600 °C heating treatment temperatures (HTTs) were described. Plant biomass and animal waste biochars exhibit large physicochemical heterogeneity due to variations in biomass chemistry and combustion conditions.This categories 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. The biochars that derived from plant residue and animal waste sorbing DEP was been investigated by batch equilibration and kinetics experiment.

## Introduction

It has been reported that biochar has the strong sorption affinity with organic compounds and may play an important role in controlling organic pollutants in the environment [1]. Biochar derived from carbon-rich biomass is defined as the solid residue of incomplete combustion and has attracted much international attention [2, 3]. A widely accepted conceptual approach to represent the transient physical chemical transitions properties of biochar is based on the gradual increase in aromaticity observed for the heat charring transformation of biomass into biochar [4]. And these fractions with different physical properties could determine the sorption behavior of biochar. It was showed that soil amended with rice or wheat-straw derived biochar enhanced sorption of diuron and atrazine [5]. It was also reported that dairy-manure can derived into biochar to effectively sorb metal and organic contaminants[6]. The biochar sorbing aromatic contaminants is mainly assisted by π-π electron donore-acceptor (EDA) interaction, pore-filling mechanism and hydrophobic interaction [7]. However, to our knowledge, a few work were available for the comparison of organic contaminants sorption by plant residue and animal waste derived biochar and the associated underlying mechanisms. DEP has been classified as a possible human carcinogen by the U.S. EPA. In a previous work, sorption of DEP to agricultural surface soil was investigated. With this in mind, it is urgently required that developing an effective and cheap sorbent for engineering application to reduce the risks of this hazardous compound in environment. However, few information is available for DEP sorption by biochar. Sorption of the DEP on biochar can be a pivotal interaction that determines its fate and behavior in the both soil and aquatic environment.

The primary objective of this study is to integrate physical and chemical information into a comprehensive model of plant residue and animal waste derived biochar. In addition, we elucidate the possible sorption mechanism between DEP and biochars and evaluate the performance of plant residue and animal waste derived biochars for engineered sorbent materials. We expect that the results of this study can increase our understanding on how the biochars with various carbonization degrees influence their sorption behaviour. These informations will be helpful for the use of various biochars as engineered sorbents for environmental applications to reduce the risk of DEP.

## Materials and methods

Six biochars were produced by the pyrolysis of plant residue and animal dung as reported[8]. The properties of these biochars were determined using elemental and gravimetric analysis, BET-$CO_2$ surface area measurements, Fourier-transform infrared (FT-IR) spectroscopy. To get information on chemical composition of biochars, their solid–state cross-polarization magic angle spinning ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were obtained using a Bruker Avance 300 NMR spectrometer (Karlsruhe, Germany) operated at a ^{13}C frequency of 75 MHz and a magic angle spinning rate of 12KHz. DEP (with a purity of > 98%) was purchased from Dr. Ehrenstorfer GmbH. A batch equilibration was conducted in 15-mL glass centrifuge tubes. The stock solution was diluted sequentially to a series of concentrations distributed evenly on a log scale 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) and shaken for 10 d at room temperature (25 ºC). The kinetics of DEP sorption by selected biochars was also performed using batch experiments in screw cap vials. Samples were taken at 0.5, 1, 2, 4, 8, 12, 24, 48, 72, 120, 168 and 240 h. The Dubinin–Ashtakhov model (DAM) were employed to fit the equilibrium sorption data of DEP by biochars.

$$\log q_e = \log Q^0 + (\varepsilon / E)^b \tag{1}$$

The pseudo first- and second-order models and two-compartment frist order sorption model have widely been used to describe sorption kinetics of sorbates. Two-compartment first order model:

$$\frac{q_t}{q_e} = f_1(1 - e^{-k_1 \cdot t}) + f_2(1 - e^{-k_2 \cdot t}) \tag{2}$$

## Results and discussion

**Characteristics of biochars.** The properties including elemental composition and ratios, ash contents, $CO_2$-SA, and pore volume of all biochars are listed in Table 1. The ash content of all the biochars varied greatly and ranged from 12.5% to 67.4%. Yields of the animal waste biochars were higher than that of plant residue biochars. The four plant residue biochars had a medium-C biochar content varied from 60% to 80%, which is consistent with reports that biochars from wood residue at high temperatures (>500 °C) generally belong to high-C biochars [9]. But the animal waste biochars obtained at 600 °C were low C biochars due to the high amount of ash (59.4–67.4%). The ((O + N)/C) of all biochars was used to index the surface polarity for these biochars, suggesting that the O-containing polar groups of the minerals within biochars were likely the major contributor to their surface polarity.

Table 2. The properties of biochars

| Sample | Component, wt% | | | | | Atomic ratio | | | $CO_2$-SA | PV (cm³/g) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Yield | Ash | C | H | O | N | H/C | O/C | (O+N)/C | |
| PL | 31.3 | 25.4 | 64.7 | 2.7 | 9.8 | 4.5 | 0.50 | 0.11 | 0.17 | 396.5 | 0.16 |
| PW | 27.9 | 12.5 | 76.5 | 2.9 | 8.0 | 0.0 | 0.41 | 0.07 | 0.07 | 378.2 | 0.16 |
| RS | 33.4 | 33.2 | 65.4 | 2.3 | 5.5 | 0.8 | 0.40 | 0.06 | 0.08 | 407.2 | 0.14 |
| MS | 27.2 | 19.8 | 70.9 | 3.7 | 5.6 | 1.0 | 0.56 | 0.05 | 0.06 | 537.6 | 0.19 |
| SD | 55.7 | 59.4 | 35.5 | 1.8 | 7.9 | 2.5 | 0.61 | 0.17 | 0.23 | 200.8 | 0.07 |
| CD | 60.2 | 67.4 | 30.6 | 0.5 | 1.1 | 1.1 | 0.60 | 0.18 | 0.26 | 255.7 | 0.09 |

PL (poplar leaf); PW (pine wood); RS (rice straw); MS (maize straw); SD (swine dung); CD (cow dung).

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 surface polarity of biochars was positively related to their ash contents, showing that the ash greatly influence the surface polarity of biochars [8]. The plant residue biochars belonged to high- or medium-C biochars and the animal waste biochars were low-C biochars. The ^{13}C NMR spectra was used to better understand the functional groups of the biochars. The soild-state ^{13}C NMR spectra of the various biochars (except for cow dung derived biochar) was showed in Figure 1. The heterogenous structures of these biochars were indicated by the different distribution of carbon functionalities (Figure 1).
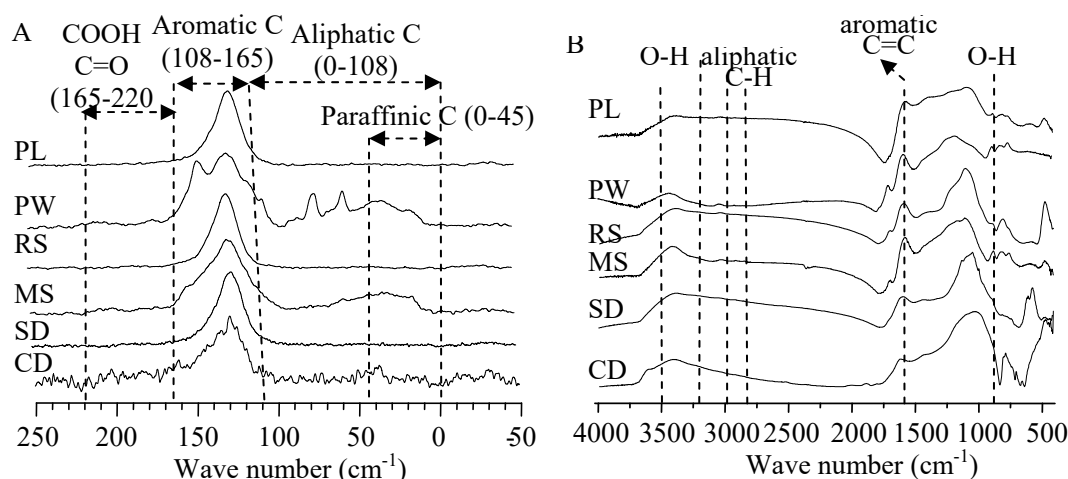
Figure 1. $^{13}C$ nuclear magnetic resonace spectra (A) and stacked FT-IR spectra (B) of biochars.

It is necessary to determine the C balance and sequestration potential of biochar management for providing a measure for the total amount of organic carbon that is added to the soil via char addition. Moreover, the composition of the parent biomass and the process conditions under which the biochar is produced is also a good indicator for engineering application.

**Sorption behavior for Diethyl phthalate (DEP).** The isotherms are presented in Figure 2 and the fitting parameters are listed in Table 3. In order to investigate the influence of such biochar properties on the sorption capacity of DEP, the sorption parameters ($Q^0$ and $b$) were correlated to additional properties of the two groups of biochars. The plant residue biochars have greater sorption capacity $Q^0$ for DEP than animal waste biochar. The ash content of the animal waste biochars was observed to be negatively related to their $Q^0$ values while the inverse trend was found for the plant residue biochars, indicating that the minerals of biochars have the effect on their sorption for DEP. The ash associated with the biochars suppress the DEP sorption.

Table 3. Fitting results of the isotherm parameters by Dubinin–Ashtakhov model (DA).

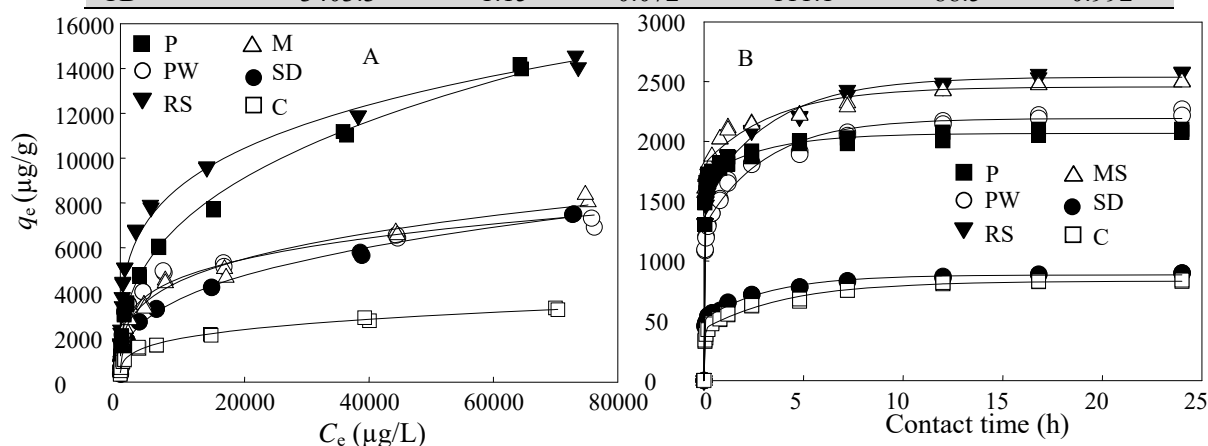| Samples | $Q^0$ | $b$ | SEE | $Q^0_{OC}$ | $Q^0/SA$ | $r^2_{adj}$ |
|---|---|---|---|---|---|---|
| PL | 9722.0 | 1.57 | 0.114 | 102.5 | 55.3 | 0.986 |
| PW | 5989.6 | 3.19 | 0.289 | 70.9 | 42.5 | 0.976 |
| RS | 13335.2 | 1.62 | 0.120 | 224.9 | 32.8 | 0.984 |
| MS | 8602.0 | 1.52 | 0.068 | 107.7 | 16.0 | 0.991 |
| SD | 5721.7 | 1.06 | 0.050 | 442.3 | 78.3 | 0.996 |
| CD | 3403.3 | 1.15 | 0.072 | 111.1 | 88.5 | 0.992 |



Figure 2. The sorption isotherms (A) and kinetics (B) of DEP by biochars.

Sorption kinetics of DEP by selected biochars are presented in Figure 2, and the data were fitted with pseudo first-, second order models and two-compartment first order sorption model. It was apparent that kinetic sorption data of DEP by selected biochars were better fitted with two-compartment first order sorption model relative to pseudo first- and second order models as

indicated by higher $r^2_{adj}$ values (Table 4). In addition, the pseudo first- and second order models were not able to represent the data at longer time points because the general underestimation of slow sorption [10]. The fitting results were consistent with previous works, where two-compartment frist order sorption model (with rapid and slow sorption compartment) has been widely used due to its agreement with multi-domain sorption theories and simplicity over other models [11].

Table 4. Parameters of kinetic sorption model.

| Sample | PFOM | | | PSOM | | | Two-compartment frist order sorption model | | | | |
|--------|------|------|-------------|------|-----------|-------------|---------|------|------|-----------|-------------|
| | $q_e$ | $K_{1a}$ | $r^2_{adj}$ | $q_e$ | $K_{2a}^{*}$ | $r^2_{adj}$ | $q_e$ | $f_1$ | $f_2$ | $K_1/K_2$ | $r^2_{adj}$ |
| PL | 1752.92 | 0.98 | 0.770 | 1798.84 | 1.24 | 0.874 | 1891.12 | 0.58 | 0.42 | 114.78 | 0.996 |
| PW | 1899.81 | 0.83 | 0.794 | 2012.94 | 1.10 | 0.895 | 2225.25 | 0.59 | 0.41 | 115.26 | 0.992 |
| RS | 2344.53 | 0.79 | 0.689 | 2520.81 | 0.90 | 0.807 | 2992.09 | 0.51 | 0.49 | 174.28 | 0.996 |
| MS | 2197.26 | 1.79 | 0.877 | 2283.50 | 2.79 | 0.940 | 2487.01 | 0.73 | 0.27 | 140.11 | 0.990 |
| SD | 930.70 | 2.01 | 0.940 | 988.67 | 3.60 | 0.972 | 1098.85 | 0.82 | 0.18 | 92.84 | 0.994 |
| CD | 695.78 | 0.51 | 0.770 | 747.24 | 0.64 | 0.880 | 842.16 | 0.52 | 0.48 | 89.95 | 0.992 |

The values of $k_1/k_2$ varied from 89 to 140, suggesting evident sorption characteristics of the fast compartment (with the higher rate constant, $k_1$) and the slow compartment (with the lower rate constant, $k_2$). The fractions of "slow" compartment ($f_1$) in the range of 0.51-0.82 and always higher than the "fast" compartment ($f_2$: 0.18-0.49). The contribution of different compartments to the overall DEP sorption also varied greatly depending on the diverse characteristic of these biochars. The fast compartment could be attributed to the exposed surface functional groups of biochars. The slow compartment may be these sorption sites in inner pores. Reduction in sorption rate of DEP by selected biochars with increasing contact time can be a result of gradual saturation of sorption sites.

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