Contributions of Different Biomass Components to the Sorption of
1,2,4-Trichlorobenzene under a Series of Pyrolytic Temperatures

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ABSTRACT

In order to investigate contributions of cellulose (CEL), hemicellulose (HEM), lignin (LIG) to the sorption capacity of biochar derived from lignocellulose, the individual component and their artificially modeled biomass mixture (C-H-L) were pyrolyzed under oxygen-limited condition at various pyrolytic temperatures (i.e. 250, 350, 500, 700 °C). The characterization analysis of biochars and sorption batch experiments were carried out. Variations in physiochemical property of different component biochars resulted in discrepancies in their ability to function as sorbents to 1,2,4-trichlorobenzene (1,2,4-TCB). The maximum mass sorption capacity (Q_{fm}) of 1,2,4-TCB was the greatest on CEL biochars ranging from 58.31 to 601.20 mg g⁻¹, and can be best explained by their huge surface area and micropore volume. Hydrophobic partitioning-sorption into ‘soft’ amorphous alkyl carbon may account for the second greatest Q_{fm} (45.09-56.57 mg g⁻¹) on HEM biochars under low pyrolytic temperatures (250-350 °C) with the lowest surface area. LIG biochars with more compact and smooth aromatic structure surface may undergo a surface monolayer specific adsorption. The Q_{fm} (87.86-196.53 mg g⁻¹) on C-H-L biochars were largely dependent on CEL and HEM components for their outstanding sorption capacity and higher content in biomass. Therefore, the results highlighted the importance of CEL and HEM components for 1,2,4-TCB sorption to biochar.

Key Words: Cellulose; Hemicellulose; Lignin; Biochar; Sorption; Hydrophobic organic contaminant

1. Introduction

In recent years, biochar has become one of the most important environmental sorbents for its strongly adsorbing the organic contaminants and inorganic heavy metals from soil and water (Qian and Chen, 2013; Lattao et al., 2014; Inyang and Dickenson, 2015; Mohan et al., 2014; Tan et al. 2015). Biochar pyrolyzed at different heat treatment temperature (HTT) and originated from different feedstock exhibited large discrepancies in the sorption capacity for contaminants (Ahmad et al., 2014; Chen and Chen, 2009; Wang et al., 2015). Presently, several researchers have studied the pyrolysis of a number of lignocellulosic biomass, such as agriculture waste, woody and herbaceous plants as sorbents to hydrophobic organic compounds (HOCs) (Zhang et al., 2011; Ahmad et al., 2012; Sun et al., 2012; Lattao et al., 2014). It revealed the importance of surface area, porosity, hydrophobicity and aromaticity of biochar for the sorption behavior of HOCs. Lignocellulosic biomass is a complex organism and it is well established that cellulose (38-50%), hemicellulose (23-32%) and lignin (15-25%) are three main organic components in general lignocellulosic biomass constituting about 90% of the total content of biomass (McKendry, 2002; Gani and Naruse, 2007; Wang et al., 2011; Zhao et al., 2014). In lignocellulose, cellulose is consisted of long chain polysaccharides without branches, while hemicellulose, including various saccharides, has a random and amorphous structure with many branches. Lignin is a heterogeneous aromatic rings polymer, thermally more stable than the former two and relatively non-reactive because that the decomposition of lignin monomers occurred above 973 K (Yang et al., 2007;

Mussatto et al., 2008; Van de Velden et al., 2010). Previous researchers have discovered that the three components undergo distinct pyrolysis process and play important roles in the property evolution of lignocellulose-based biochar (Yang et al., 2007; Cagnon et al., 2009; Lv et al., 2013; Xu and Chen, 2013). Therefore, they should contribute to the different sorption behaviors of biochar depending on their respective intrinsic chemical composition, structure and mass proportions in lignocellulosic biomass.

Recently, efforts have been made to investigate the property variations and the sorption capacity of cellulose or lignin after pyrolysis (Wang and Xing, 2007; Cotoruelo et al., 2009; Li et al., 2014; Lorenc-Grabowska and Rutkowski, 2014b). Some researchers revealed that lignin is probably the main component of lignocellulosic precursors responsible for the micropores of activated carbons (Suhas et al., 2007; Cagnon et al., 2009; Tiryaki et al., 2014). Lorenc-Grabowska and Rutkowski (2014a) reported that the activated carbons derived from cellulose could develop micropores predominantly, while the lignin-based activated carbons were characterized by both micro and mesoporous structure. They also reported that activated carbon from cellulose had higher sorption capacity than that from coconut shell as the sorbent to phenol (Lorenc-Grabowska and Rutkowski, 2014b). Wang and Xing (2007) revealed that the sorption of phenanthrene and naphthalene to chitin and cellulose was greatly increased after charring due to their enhanced surface area, porosity and aromatic components. In addition, it is revealed that aliphatic hydrocarbons from cellulose could be converted into aromatic components by

pyrolysis (Wang and Xing, 2007; Rutherford et al. 2012). Li et al. (2014) further compared the surface characteristics and sorption properties of cellulose, lignin and wood charring at 400-600 °C to identify that the sorption capacity of nitrobenzene on lignin biochar was comparable to that both on cellulose and wood biochars. However, the pyrolytic effect of hemicellulose, which is the second most abundant renewable polymers in nature (Lv et al. 2010), on the sorption property of biochar has not been particularly concerned. In addition, some researches have discovered that interactions among different biomass components occurred in the pyrolysis process (Hosoya et al., 2007; Giudicianni et al., 2014; Zhao et al., 2014). However, it is not well understood whether the interaction could modify the sorption behavior of biochar relative to a single biomass component based biochar. Therefore, with respect to distinct variations of cellulose, hemicellulose and lignin in the pyrolysis process, there is a need for an illustration of the sorption capacity and sorption mechanism of biochar derived from individual component and their synthetic mixture together proportionally under different HTTs.

Chlorinated aromatic hydrocarbons (CAH) are widely used as agrochemicals, degreasers and feedstock for synthesis of other substances. They have been priority contaminants in China which have been detected in water, sediment, soil and sewage sludge (Song et al., 2013; Yang et al., 2014). In the present paper, 1,2,4-trichlorobenzene (1,2,4-TCB) was selected as a common representative of CAH for the sorption study. Selected physicochemical properties of 1,2,4-TCB are presented in Table S1. 1,2,4-TCB is an apolar sorbate that normally condenses as

liquid at 25 °C (Zhu et al. 2004; Nguyen et al., 2007). Cellulose (CEL), hemicellulose (HEM), and lignin (LIG) and their artificially modeled biomass mixtures (C-H-L) were pyrolyzed under oxygen-limited condition ranging from 250 to 700 °C, following which their characterization and sorption experiments for 1,2,4-TCB were undertaken. The major objectives of the study are to (1) evaluate variations in the physiochemical property of individual component based biochar and potential interactions with each component in C-H-L based biochar; (2) compare different contributions of the three components simulated biochar as sorbents to 1,2,4-TCB; and (3) interpret main mechanisms controlling the differences in sorption properties among the three components.

2. Materials and experimental methods

2.1 Materials

Biochar was synthesized from individual CEL, HEM, LIG and C-H-L. The mass ratio of CEL, HEM and LIG was 4:3:2 in C-H-L to model the organic composition of corn stock and bamboo biomass (Lv et al., 2013; Cao et al., 2014). Commercial CEL and alkali LIG were sourced from Sigma Aldrich and Ruibio, respectively. Xylan, selected as a model compound for HEM, was purchased from the domestic Reagent Co. 1,2,4-TCB with purity greater than 99% were purchased from Sigma Aldrich Chemical Co. The materials mentioned above were used as received.

2.2 Pyrolysis of samples

The four precursors were pyrolyzed individually at 250, 350, 500 and 700 °C (C-H-L at 350, 500 and 700 °C) under oxygen-limited conditions to simulate the

pyrolysis of biomass in natural environment using a reported method (Chen et al., 2008; Chen et al., 2012; Qian et al., 2013). Briefly, Samples were tightly packed into a porcelain crucible, covered with a fitted lid and pyrolyzed in a muffle furnace. The programmed temperature rate was adjusted to $5^{\circ}\text{C min}^{-1}$ and the holding time was 6 h. The biochar yield was measured by the proportion of charred residues to the original precursor. Consequently, samples were grounded to pass through a 0.154-mm sieve and stored in glass bottles. The sample was labeled as the relative abbreviation of precursor and pyrolytic temperature, for example, CEL250 for CEL pyrolyzed at 250°C .

2.3 Characterization of Samples

Thermogravimetric Analysis (TGA) was performed using a TG analyzer (DTG-60H, Japan) under nitrogen atmosphere with a flow rate of 100 mL/min. The temperature was heated from room temperature to 800°C at 10°C/min . The elements of samples including C, N, H and S were performed using an elemental analyzer (Vario Macro CHNS-O-CL, Elementar, Germany). The combustion temperature was 1100°C . The content of O was determined by mass difference. Atom ratios of H/C and O/C were calculated. The ash content was measured using a muffle furnace at 800°C for 6 hours. ASAP 2020 system (Micromeritics, Norcross, GA, USA) was used to measure surface and porous structure of biochars (Nguyen et al., 2007; Li et al., 2014). The functional groups of samples were determined using a Nicolet Fourier transform infrared (FTIR) spectrophotometer (Nicolet iS10, Thermo scientific, USA) in KBr wafers (1%). The scanning region ranged from 400 cm^{-1} to 4000 cm^{-1} with a

resolution of 1.0 cm^{-1} and 64 scans (Chen et al., 2008). Zeta potential (ζ) was measured on a zetasizer (ZetaPlus, Brookhaven, USA). The methods were detailed in the Supporting Information.

2.4 Sorption experiments

The working solution was prepared with ultrapure water and 1,2,4-TCB was dissolved in methanol (>99%) to formulate stock solutions. In order to make sure the accuracy and reliability of collected data, all batch tests including blank controls, were performed in 20 mL glass vials equipped with Teflon-lined screw cap. The measured biochar sample (~1-8 mg) was first mixed with 19 mL of a background solution containing 0.005 M CaCl_2 and pre-wetted for 12 h. Accurate volume of a stock solution was then added to sample vials using a glass micro-syringe with the volume percentage of methanol less than 0.1% (v/v) (Nkedikizza et al., 1987). The vials were sealed immediately with a cap and placed on a reciprocating shaker, agitating at 150 rpm at 25 °C. In the sorption kinetic experiment, the initial concentration of 1,2,4-TCB was approximately $1000\text{ }\mu\text{g L}^{-1}$ and the time periods ranged from 4 h to 72 h. In the sorption isotherm experiment, the concentration of 1,2,4-TCB was in the range of 500 to $5000\text{ }\mu\text{g L}^{-1}$. 1,2,4-TCB from the aqueous phase was extracted with hexane and quantified with the 7890 GC/5973 MSD instrument (Agilent Technologies, Palo Alto, CA). The details of sorption experiments were provided in the Supporting Information.

2.5 Data Analysis

The pseudo-first-order kinetic model and pseudo-second-order kinetic model

were employed to analyze sorption kinetics of biochars. The Freundlich, Temkin, Langmuir and Polanyi-Manes isotherm model were used to fit the sorption isotherms. These models were detailed in the Supporting Information.

3. Results and discussion

3.1 Characterization of biochar

The thermogravimetric analysis curves of CEL, HEM, LIG and C-H-L sample were presented in Fig. 1a. CEL, HEM and LIG were decomposed at different rates and within distinct temperature ranges. LIG was the most difficult to decompose in the HTT range (~ 30 - 800 °C) with the highest solid residue (~ 53 wt.%). The maximum mass loss rate was $0.61 \text{ wt.\% min}^{-1}$ at 210 °C. The pyrolysis of HEM started at the lowest temperature. Its weight loss mainly happened at 191 - 320 °C with the maximum mass loss rate of $10.96 \text{ wt.\% min}^{-1}$ at 304 °C, and the solid residue was approximately 13 wt.% at 800 °C. The decomposition temperature of CEL mainly ranged from 271 to 386 °C with the maximum weight loss rate of $24.96 \text{ wt.\% min}^{-1}$ at 348 °C. The solid residue of CEL could be ignored when the HTT was higher than 600 °C. Therefore, the pyrolysis characteristics of the three components were well consistent with those reported by Yang et al. (2007) who also discussed the energy consumption properties of the three components with differential scanning calorimetry (DSC) method. It could be concluded that the pyrolysis of CEL was endothermic, while HEM and LIG showed an exothermal reaction. The pyrolysis behavior of C-H-L was among CEL, HEM and LIG with the weight loss mainly ranging from 109 to 390 °C and about 25 wt.% of solid residue was left after

pyrolysis. The maximum mass loss rate was 4.42 wt.% min⁻¹ at 179 °C and 3.34 wt.% min⁻¹ at 329 °C.

Table 1 reports the yield, elemental composition, ash, and atomic ratio (H/C and O/C) of the thirteen biochars. LIG biochars gave the highest yields (64.32-84.51%) within the HTT range due to its stable thermal property and recalcitrant components. The crystallization of LIG seems to appear in the charring process at 700 °C resulting in the biochar with hard gray inner core (Fig. S1a). The yields of CEL biochars were between 26.43% and 57.43% at low HTTs (250-350 °C) and maintained relatively stable at about 16.60% at moderate to high HTTs (500-700 °C). The carbonized HEM was characterized by irregular honeycomb ball-like carbon with macropores and had gloss like caramel (Fig. S1b, c). This may be associated with abundant saccharides in HEM polymers (Lv et al., 2010). The yields of HEM biochars ranged from 19.84% to 56.59% at low HTTs (250-350 °C). However, the biochar from HEM above 500 °C could not be obtained due to complete decomposition. It is observed that HEM biochar overflowed the crucible after carbonization both at 250 and 350 °C (Fig. S1b). As a result of the exothermal reaction of HEM in pyrolysis and its least thermally stable property among the three components (McKendry, 2002; Yang et al., 2007), it is deduced that volume expansion and devolatilization of HEM occurred in the pyrolysis, leading to complete combustion of the residues under partial anaerobic condition with increasing HTT. In the case of C-H-L biochars, no volume expansion was observed after pyrolysis, which may be attributable to the endothermic/exothermic interaction among the components (Tiryaki et al., 2014). The

yields of C-H-L biochars were 33.30%, 22.41% and 17.88% at 350, 500 and 700 °C, respectively, similar with the pyrolysis of natural lignocellulosic materials (Chen et al., 2008; Fu et al., 2009; Luo et al., 2014). Assuming that the three components in C-H-L were pyrolyzed independently, the calculated yield equal to the yield of each component multiplied by its content in C-H-L was 36.29%, 23.30% and 21.65%, respectively, which was slightly higher than the actual yields of biochar. Hosoya et al. (2007) found that lignin could reduce the char fraction formed from cellulose by inhibiting the thermal polymerization of levoglucosan and enhancing the formation of the low molecular weight products from cellulose, while cellulose could reduce the secondary char formation from lignin. Wang et al. (2011) also revealed that interactions may occur among the three mixture components in the pyrolysis process, although the yields of char residues did not change markedly between the experimental results and the calculated results. For the determination of ash content, both CEL and HEM biochars had ignored inorganic content, however, some inorganic content was included in LIG biochars as a result of the process of LIG separation from lignocellulosic feedstock (Li et al., 2014). Additionally, C-H-L700 even showed higher amount of ash content than LIG700, indicating that the organic component was reduced markedly at higher HTT. Therefore, it is deduced that the thermal decomposition of some organic fraction may be enhanced with more volatile compounds formed in the pyrolysis of C-H-L sample, leading to increasing ash content.

Table 1 presents the C, N, H, S and O contents on ash free basis. The elemental composition for CEL and HEM are extremely similar. Their contents of C progressively increased after the carbonization accompanied by gradual decline in H and O contents. In addition, the H/C (O/C) ratio reduced accordingly. It should be noted that the discrepancies in the H/C (O/C) ratios between CEL and HEM biochar increased with the increase of HTT, as shown in the Van Krevelen diagram (Fig. 1b). Compared with CEL and HEM, more N and S contents were contained in LIG and they were lost markedly with the increase of HTT. The content of C in LIG biochars was relatively stable at approximately 40% but the content of O increased with the increase of HTT, leading to the apparent increase in the O/C ratio (Fig. 1b). It is interpreted that a recalcitrant oxygen fraction was transformed into LIG biochar in pyrolysis. Comparatively, LIG biochars had lower H/C ratios than CEL and HEM biochars (Fig. 1b), indicating greater aromaticity of LIG biochars. The H/C ratios and O/C ratios of C-H-L biochars were much closer to those of CEL and HEM biochars between 350 and 500 °C, but the O/C ratio for C-H-L700 was significantly influenced by LIG component.

The FTIR spectra of CEL, HEM, LIG, C-H-L and their biochars pyrolyzed at different HTTs are shown in Fig. 2. The FTIR signals in CEL, HEM and LIG were well in agreement with the reported results (Yang et al., 2007). They are most likely consisted of alkyl CH₂ (2900 cm⁻¹), C-H (1402 and 900-700 cm⁻¹), aromatic C=C (1650-1580 cm⁻¹), -OH (~3420 cm⁻¹), C=O (1700-1730 cm⁻¹ and 1510-1560 cm⁻¹), methoxyl-O-CH₃ (1470-1430 cm⁻¹), OH (1440-1400 cm⁻¹), C-O-C and alcohol-OH

(1279-1060 cm^{-1}). For CEL and HEM biochar (Fig. 2a), the band intensity for C=O and aromatic C=C increased in CEL250 and HEM250, and subsequently diminished at higher HTTs. With the increase of HTT, -OH, alkyl CH_2 , methoxyl-O- CH_3 , C-O-C and C-O dramatically diminished both in CEL and HEM biochar. The absorption peaks at 1222, 1238 cm^{-1} assigned to the aromatic CO- stretching gradually increased suggesting the transformation of the organic bound form of O (Chun et al., 2004; Yang et al., 2006a). For LIG biochars, the peaks at 1577, 1420 and 900-700 cm^{-1} assigned to aromatic compounds increased in LIG250 (Fig. 2c). Furthermore, LIG700 showed a much greater aromatic skeletal mode due to the formation a diversity of LIG monomers at higher HTT with stronger absorption peaks at 1420 and 900-700 cm^{-1} (Van de Velden et al., 2010). Likewise, the intensified absorption peak at 1150 cm^{-1} for LIG biochar was accompanied by the increase of O content (Table 1), which may be associated with the crystallization of LIG. C-H-L displayed FTIR signals similar to CEL because of higher content of CEL contained in it (Fig. 2d). However, moderate signals at 1696 and 1636 cm^{-1} from CEL and HEM were contained in C-H-L350, in comparison to strong signals at 1447, 1149 and 900-700 cm^{-1} from LIG component. Furthermore, most functional groups assigned to aliphatic hydrocarbons were lost or transformed into aromatic composition at high HTT, making the surface chemical properties of C-H-L500 and C-H-L700 well in agreement with that of LIG biochar at corresponding HTTs. Previous studies indicated that LIG could interact with CEL or HEM in the pyrolysis, resulted in the generation of gas, bio-oil and char residue phase to redistribute in the products (Hosoya et al., 2007; Wang et al., 2011; Giudicianni et

al., 2014). Therefore, it is deduced that the presence of LIG may promote the decomposition of CEL and HEM but reduce their carbonization in the pyrolysis of C-H-L samples.

The data of BET-specific surface area (SA), micropore area (t-Plot MA), total pore volume (TPV), micropore volume (t-Plot MPV) and adsorption average pore diameter (APD) is presented in Table 2. The nitrogen adsorption-desorption isotherms of various biochars is shown in Fig. S2. The SA and TPV of different components all gradually enhanced with the increase of HTT except LIG biochars. CEL biochars between 350 and 700 °C was mainly consisted of microspores (<2 nm) based on their t-Plot MPV (62.59-285.41 mm³ g⁻¹) and APD (1.62-1.87 nm) data. The pore size distribution obtained with BJH method (Fig. S3) and the APD data for the other biochars indicated that they mainly contained mesopores (2-50 nm) and macropores (>50 nm). CEL biochar had the greatest enhancement in SA (5.89-725.84 m² g⁻¹) and TPV (13.43-293.40 mm³ g⁻¹) from 250 to 700 °C. That was markedly higher than those reported for cellulose-based biochars (Wang and Xing, 2007; Li et al., 2014). This is also compared favorably with the biochars obtained from pine wood and other various lignocellulosic precursors with the maximum SA of 637 m² g⁻¹ (Chen et al., 2012; Ahmad et al., 2014). On the contrary, HEM biochars had the lowest SA (0.46-0.55 m² g⁻¹) and TPV (0.76-0.98 mm³ g⁻¹), in agreement with the visible macropores in the charring HEM (Fig. S1c). LIG biochars also showed a poor development in SA (0.99-11.17 m² g⁻¹), in which the SA of LIG350 (2.72 m² g⁻¹) was similar to the result (2.59 m² g⁻¹ for LIG330) reported by Hu et al. (2014). However,

the SA of LIG700 decreased to $1.60 \text{ m}^2 \text{ g}^{-1}$, which may be associated with the crystallization of LIG at 700°C as mentioned above. The SA of C-H-L biochars in the range of $1.14\text{--}184.91 \text{ m}^2 \text{ g}^{-1}$ was apparently less than the calculated value (69.85 , 195.50 and $322.95 \text{ m}^2 \text{ g}^{-1}$) on the basis of the mass fraction of each component. It is deduced that the inhibition of the carbonization of CEL may cause the noticeable decline in the development of SA in C-H-L biochars.

Fig. S4 illustrates the pH-dependent Zeta potential (ζ) curves for various biochars. The ζ monotonically decreased with the increase of solution pH. Biochars prepared at higher HTT had greater ζ at the same solution pH. The point of zero charge (pH_{pzc}) for biochars pyrolyzed between 350 and 700°C were all less than 2.0 . The biochar particles will carry negative surface charges in the case of the solution $\text{pH} > \text{pH}_{\text{pzc}}$. The variation in ζ as a function of pH for C-H-L350 and C-H-L500 was closer to CEL and HEM biochar, while C-H-L700 was affected by LIG700 apparently.

3.2 Uptake of 1,2,4-TCB by various biochars

Sorption kinetic experiments. The amount of 1,2,4-TCB sorbed onto various biochars at different contact time were depicted in Fig. 3. The apparent equilibrium times were 48 h for the tested biochars. The sorbed amount of 1,2,4-TCB decreased in the order of $\text{CEL700} > \text{CEL500} > \text{C-H-L700} > \text{CEL350} > \text{HEM350} \approx \text{C-H-L350} > \text{LIG350} > \text{LIG700}$ under sorption equilibrium. The sorption kinetic data were well fitted with the pseudo-second-order model (Table S2 and Fig. S5). The pseudo-second order model assumed that chemical sorption involves valence forces through sharing or exchange of electrons between the sorbent and the sorbate (Mayakaduwa et al., 2016).

The coefficients (R^2) for pseudo-second-order kinetic model were between 0.985 and 0.999. The rate constant (k_2) increased with the increase of HTT for each type of component biochar, with the lowest k_2 value for HEM350 biochar ($0.07 \times 10^{-3} \text{ g } \mu\text{g}^{-1} \text{ h}^{-1}$) and the greatest k_2 value for LIG700 ($1.11 \times 10^{-3} \text{ g } \mu\text{g}^{-1} \text{ h}^{-1}$). The k_2 for C-H-L biochars were between that of HEM and CEL biochars, which may be influenced by higher contents of CEL and HEM in C-H-L. Therefore, noticeable differences in the sorption rates of biochars from CEL, HEM and LIG indicated the different contributions to the sorption kinetic of biochar from lignocellulose. The sorption kinetic properties of C-H-L biochars should be a function of combined the interactions among the three components.

Sorption isotherm experiments. Sorption isotherms of 1,2,4-TCB on biochars from CEL, HEM, LIG and C-H-L with Freundlich, Temkin and Langmuir fitting lines, respectively, are presented in Fig. 4a-d. Regression parameters are illustrated in Table S3. The data was best fitted with Freundlich model ($R^2=0.931-0.990$) except LIG biochars ($R^2=0.873-0.919$), for which Langmuir model could better fit the sorption isotherms ($R^2=0.887-0.969$). Freundlich isotherm is widely used to describe sorption occurring on heterogeneous and amorphous surfaces with non-uniform energy distribution, while Langmuir isotherm is mainly employed to monolayer adsorption on homogeneous surface (Yan et al., 2008). LIG is a phenolic polymer and the strengthening component of a cell wall, which could be transformed into the condensed aromatic core structure. LIG chars were rich in mesopores and macropores (Table 2) and had smooth surfaces (Kang et al., 2012; Lv et al., 2013). Therefore,

1,2,4-TCB sorption to LIG biochars may undergo a different mechanism from that to CEL and HEM biochars. It is more likely that LIG biochars contacted with 1,2,4-TCB by surface monolayer adsorption, while CEL and HEM biochars captured 1,2,4-TCB by heterogeneous multilayer sorption. The sorption isotherm was also well fitted to Temkin model ($R^2=0.832-0.985$) indicating that 1,2,4-TCB sorption to biochars could be a chemisorption process.

As shown in Table S3, the maximum mass sorption capacity (Q_{fm}) was determined using the Freundlich model with the aqueous solubility of 34.6 mg L^{-1} for 1,2,4-TCB. With respect to the type of precursor, the CEL biochar had the highest Q_{fm} ranging from 58.31 to 601.20 mg g^{-1} , followed by HEM biochar from 45.09 to 56.57 mg g^{-1} and LIG biochar from 6.94 to 22.51 mg g^{-1} . The Q_{fm} for LIG biochar was approximately one order of magnitude less than that for CEL biochar. LIG700 showed an abnormal result with the sorption capacity fell less than that of LIG500 and LIG350. The low SA and t-plot MV and the increase in O/C ratio were most likely be responsible for the apparent decline in the sorption capacity, although it had the highest aromaticity among the thirteen biochar samples (Table 2). Li et al. (2014) also reported that LIG pyrolysis at 600°C exhibited lower sorption capacity than that at 400°C when the ratio of C_e/C_s (C_s = aqueous solubility) was greater than 0.1. Thus, it is deduced that the crystallization at high HTT restrained the porosity development, leading to LIG biochar much compact. In addition, the amount of 1,2,4-TCB sorbed onto CEL biochar was much higher than those reported results from the literatures (Wang and Xing, 2007; Li et al., 2014). Apart from the huge SA and t-Plot MV

obtained in CEL biochars, the steric hindrance of the sorbate solutes should be taken into account, as nitrobenzene, naphthalene and phenanthrene having greater or similar molecular volume (i.e. 0.213, 0.159 and 0.212 nm³) than 1,2,4-TCB (0.160 nm³). Therefore, it could be concluded that CEL and HEM displayed greater sorption capacity than LIG as sorbents to 1,2,4-TCB after charring. The greatest Q_{fm} of 1,2,4-TCB on CEL biochar demonstrated that CEL had the obvious advantage in contribution to biochar as a strong sorbent. For biochars derived from modeled biomass, the Q_{fm} on C-H-L350, C-H-L500 and C-H-L700 was 87.86, 125.85 and 196.53 mg g⁻¹ (Table 3), respectively, which was closer to the Q_{fm} onto CEL and HEM biochar. The corresponding calculated Q_{fm} (98.28, 228.73 and 269.21 mg g⁻¹) according to the proportion of each component was higher than the model results with experimental data. Similarly, the lower sorption capacity onto C-H-L based biochar may be attributed to the interactions among the three components and the inhibition of the carbonization of CEL.

3.3 Influence of biochar property on the sorption

To explore the influence of biochar properties on the sorption behavior, the relationship between the Q_{fm} and the physiochemical property of biochar was analyzed. The possible influence factors include SA, t-Plot MV, aromaticity and hydrophobicity of the biochar. The statistical change of the Q_{fm} with SA (t-Plot MV) of biochars is presented in Fig. 5a (Fig. S6a). The Q_{fm} was linearly correlated with the SA (t-Plot MV) with $R^2=0.984$ ($R^2=0.983$). Particularly, greater SA and huge t-Plot MV developed in biochar at high HTT could provide ample accessible sites and

porosity selection to 1,2,4-TCB (critical molecular size=4.9 Å in Table S1). In addition, the increased micropores in biochars would be responsible for their enhanced nonlinearity of sorption isotherms for 1,2,4-TCB. Thus, the results demonstrated that the surface adsorption and available pore-filling mechanism as a critical factor controlled the sorption capacity. However, the sorption capacity of HEM biochar and C-H-L350 actually did not comply with the pattern because they had smaller SA and t-Plot MV than those of LIG350 but higher Q_{fm} (the insert figure in Fig. 5a and Fig. S6a). Clearly, SA or t-Plot MV alone is insufficient to explain the sorption data, and other properties must play important roles in HEM and C-H-L biochar at low HTTs.

To further investigate the influencing factors, the relationship between the surface area-normalized maximum mass sorption capacity ($Q_{fm,SA}$) and H/C (O/C) ratio was compared. As presented in Fig. 5b and Fig. S6b, no apparent correlation between the $Q_{fm,SA}$ and the H/C (O/C) ratio was observed, suggesting that the aromaticity and hydrophobicity of biochar were not significant contributors to the sorption behavior of biochar. It should be noted that at a given equilibrium concentration, the sorbed amount of 1,2,4-TCB to each biochar did not coalesce, indicating that multiple factors may affect the sorption. The HEM biochars with the highest $Q_{fm,SA}$ demonstrated its distinct sorption mechanism apart from surface adsorption or pore-filling sorption. Compared with CEL and LIG, HEM including various saccharides, has a random and amorphous structure with many branches (Yang et al., 2007). Biochars from HEM at 250 and 350 °C with predominant alkyl

carbon structure (Fig. 2b) and relative lower O/C ratios (Table 1) may cause additional sorption reaction, such as the significant partitioning-sorption, because that the swollen HEM biochar showed the lowest sorption rate (Table S2), as Chen et al. (2012) reported that the decreased diffusion of the solute into the incomplete carbonized organic matter, result in a slow sorption rate for biochar prepared at 250 and 350 °C. Therefore, the sorption of 1,2,4-TCB to C-H-L350 may also be markedly influenced by the presence of HEM component. The importance of amorphous aliphatic carbon in biochar for the sorption of phthalic acid esters (PAEs) with $\log K_{ow}$ (2.42-4.70) similar to that of 1,2,4-TCB (4.05) was also revealed by Sun et al. (2012), who reported that biochar synthesized under relative low HTTs (300-400 °C) demonstrated the maximum sorption strength. It was also identified that the sorption capacity of PAEs onto grass-based biochar with lower SA was more effective than that onto wood-based biochar with higher SA (Sun et al., 2012). In addition, Chefetz and Xing (2009) reviewed the roles of aliphatic and aromatic moieties in adsorbing organic compounds and concluded that aliphatic structure had considerable superiority in HOCs-sorption in many cases. CEL biochars and C-H-L700 with the lowest $Q_{fm,SA}$ except CEL250 indicated that SA and t-Plot MV were main controlling factors influencing the sorption capacity of biochar at higher HTTs. Compared with CEL biochars, most LIG biochars showed higher $Q_{fm,SA}$ value. The sorption isotherms for LIG biochars better fitted to Langmuir model has suggested the monolayer adsorption of 1,2,4-TCB onto LIG biochars (Table S3). Considering the autogenous aromatic structures on LIG surface, it is more likely that the surface specific

adsorption may have occurred, such as $\pi=\pi$ interactions between the benzene ring in 1,2,4-TCB molecules and the autogenous aromatic structures of LIG biochar (Ma et al., 2011; Wang et al., 2014). Therefore, noticeable discrepancies in sorption mechanisms may have existed in different component biochars because of their different chemical composition and structures. The C-H-L biochars combined the multiple sorption reactions from each component, but the sorption contributions from CEL and HEM components are more significant.

The sorption isotherms were further analyzed with the Polanyi-based isotherm model to investigate the effect of surface area and porosity on the adsorption mechanism (Yang et al., 2006b). The Polanyi-based adsorption isotherms of 1,2,4-TCB by various biochars are presented in Fig. S7 and the fitting parameters are illustrated in Table S4. More 1,2,4-TCB molecules were adsorbed into the pores of CEL based biochar (Fig. S7a), as the maximum saturated sorption capacity ($\log Q_0$) was predicted with the Polanyi model (Table S4). The sorbed volume by biochar synthesized at higher HTT apparently increased because of the progressive porosity development. In the case of biochar synthesized at low HTTs (250-350 °C), the predicted Q_0 for 1,2,4-TCB exceeded the t-Plot MV or even the TPV of biochar (Table 2) except for LIG250 and LIG350. In particular, HEM250 and HEM350 had the highest exceedance. This is contradictory with the pore-filling mechanism provided that sorbents are nondeformable (Yang et al., 2006b). Most likely, some other mechanism may have affected the sorption, such as partitioning-sorption in agreement with the conclusion discussed above. In addition, certain amounts of

autogenous organic chemicals remained in the biochar occupying some pores at low HTT, implying the inaccurate measurement of pore volume (Nguyen et al., 2007; Luo et al., 2014). However, the presence of autogenous organic chemicals did not affect 1,2,4-TCB sorption into the pores of biochar as its sorption isotherms for a natural wood char and a treated wood char with no autogenous organic chemicals in it were almost identical (Nguyen et al., 2007). Therefore, it should be reasonably concluded that the partitioning-sorption mechanism played an important role in the sorption capacity of biochar at low HTTs (250-350 °C). For biochar synthesized at higher HTTs (500-700 °C), Q_0 was less than the determined t-plot MV. This may be associated with the sorbed 1,2,4-TCB molecules inaccessible to some interconnected micropores. Therefore, the partitioning-sorption may be more suitable to explain the sorption behavior of CEL and HEM biochar produced under lower HTTs (250-350 °C), surface adsorption and micropore-filling sorption should be a main controlling factor on CEL biochar, while for LIG biochars, surface specific adsorption may be a main influencing factor because of its compact, smooth aromatic structure surface and low porosity.

4. Conclusion

It is identified that CEL, HEM and LIG simulated biochar with distinct physiochemical composition and structures displayed different sorption behaviors as sorbents to 1,2,4-TCB. The sorption rate constant decreased in the order of biochar from LIG>CEL>HEM, while the Q_{fm} increased in the order of biochar from CEL>HEM>LIG. Different mechanisms may have preferentially operated on the

sorption behavior of different component-based biochars. Comparatively, 1,2,4-TCB sorption to CEL biochar was significantly controlled by surface area and micropore volume, HEM biochars synthesized at 250 and 350 °C exhibited stronger partitioning-sorption, and LIG biochars showed a marked surface specific adsorption. The sorption capacities of C-H-L biochars were largely dependent on CEL and HEM components. It is also identified that some interaction among the three components may have occurred in the pyrolysis of C-H-L sample. Therefore, CEL and HEM components had significant contributions to the biochar as the sorbent to 1,2,4-TCB dependent on their contents and sorption capacity.

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Figure Captions

Fig. 1. Thermogravimetric analyses of various components (a), the Van Krevelen diagram (b).

Fig. 2. Fourier transform infrared (FTIR) spectra of (a) CEL and their biochar, (b) HEM and their biochar, (c) LIG and their biochar, (d) C-H-L and their biochar.

Fig. 3. Sorption kinetic curves of 1,2,4-trichlorobenzene on (a) CEL and HEM biochar, (b) LIG biochar, (c) C-H-L biochar.

Fig. 4. Freundlich, Temkin and Langmuir sorption isotherms of 1,2,4-trichlorobenzene by (a) CEL biochar, (b) HEM biochar, (c) LIG biochar, (d) C-H-L biochar.

Fig. 5. The relationship between the maximum mass sorption capacity (Q_{fm}) and the BET-specific surface area (a), the relationship between the surface area-normalized maximum mass sorption capacity ($Q_{fm,SA}$) and H/C ratio of biochar (b).

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Table Captions

Table 1 Yields, elemental composition (on ash free), ash and atomic ratio of biochar.

Table 2 Porous structure of biochars.

Table 1

Yields, elemental composition (on ash free), ash and atomic ratio of biochar.

Biochar	Yields (%)	N (%)	C (%)	H (%)	O (%)	S (%)	Ash (%)	H/C	O/C
CEL	-	-	41.81	6.70	51.49	-	0.02	1.92	0.92
CEL250	57.43	-	48.82	4.95	46.23	-	0.10	1.22	0.71
CEL350	26.43	0.02	50.31	3.46	46.21	-	0.11	0.83	0.69
CEL500	17.06	0.02	57.41	4.01	38.55	-	0.11	0.84	0.50
CEL700	16.6	-	61.80	3.92	34.28	-	0.25	0.76	0.42
HEM	-	-	41.80	6.70	51.50	-	0.01	1.92	0.92
HEM250	56.59	0.01	50.19	5.36	44.44	-	0.01	1.28	0.66
HEM350	19.84	0.07	59.09	2.85	37.99	-	0.01	0.58	0.48
LIG	-	0.53	43.07	5.51	45.87	5.03	11.07	1.54	0.80
LIG250	84.51	0.34	40.57	2.61	54.33	2.15	11.21	0.77	1.00
LIG350	80.71	0.43	43.29	1.47	53.13	1.68	14.71	0.41	0.92
LIG500	70.73	0.17	40.32	1.08	57.14	1.30	23.69	0.32	1.06
LIG700	64.23	0.06	39.42	1.03	59.19	0.29	26.29	0.31	1.13
C-H-L350	33.3	0.10	59.09	3.82	36.54	0.45	13.27	0.78	0.46
C-H-L500	22.41	0.10	61.48	3.82	34.51	0.10	16.82	0.75	0.42
C-H-L700	17.88	0.04	34.01	1.52	64.35	0.08	35.05	0.54	1.42

Table 2

Porous structure of biochars.

Biochar	BET-SA (m² g⁻¹)	t-Plot MA (m² g⁻¹)	TPV (mm³ g⁻¹)	t-Plot MV (mm³ g⁻¹)	APD (nm)
CEL250	5.89	4.06	13.43	1.51	9.12
CEL350	155.38	150.68	72.49	62.59	1.87
CEL500	579.08	560.43	253.70	229.92	1.75
CEL700	725.84	722.47	293.40	285.41	1.62
HEM250	0.46	0.27	0.76	0.13	6.61
HEM350	0.55	0.40	0.98	0.19	7.14
LIG250	0.99	0.45	3.63	0.11	14.68
LIG350	2.72	0.49	13.37	0.12	19.68
LIG500	11.17	9.70	7.16	4.12	2.56
LIG700	1.60	0.52	3.38	0.24	8.44
C-H-L350	1.14	0.73	5.14	0.26	17.97
C-H-L500	7.58	4.68	8.62	2.03	4.55
C-H-L700	184.91	174.49	109.47	93.01	2.37

BET-SA: BET-surface area; t-Plot MA: t-Plot micropore area; TPV: total pore volume; t-Plot MPV: t-Plot micropore volume; APD: adsorption average pore diameter (4V/A by BET).

Modeled biomass

Pyrolysis under
oxygen-limited
condition

Biochar

MSC: Maximum Sorption Capacity
Main Mech.: Mechanism

● 1,2,4-Trichlorobenzene