



Contributions of different biomass components to the sorption of 1,2,4-trichlorobenzene under a series of pyrolytic temperatures



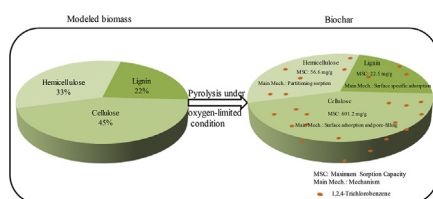
Lu Han, Linbo Qian, Jingchun Yan, Mengfang Chen*

Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China

HIGHLIGHTS

- Cellulose biochar developed the highest surface area and micropore volume.
- Cellulose and hemicellulose biochar showed higher ability in adsorbing 1,2,4-TCB.
- The sorption capacity of biochar may be depressed in the presence of lignin.
- Lignocellulose biochar depended on the ability and content of each component.
- Different components differed in the sorption mechanisms.

GRAPHICAL ABSTRACT



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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 physicochemical 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.

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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

* Corresponding author.

E-mail address: mfchen@issas.ac.cn (M. Chen).

(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 (Suhass 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 surface characteristics and sorption properties of cellulose, lignin and wood charring under 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 physicochemical 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, 2012; Qian and Chen, 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 °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[HYPHEN]O[HYPHEN]CL-, Elementar, Germany). The

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