Environmental Pollution 233 (2018) 64–70

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Correlations and adsorption mechanisms of aromatic compounds on biochars produced from various biomass at 700 °C☆

Kun Yang [a, b, c, *], Yuan Jiang [a, b, c], Jingjing Yang [a, b, c], Daohui Lin [a, b, c]

[a] Department of Environmental Science, Zhejiang University, Hangzhou 310058, China
[b] Key Laboratory of Environmental Pollution and Ecological Health of Ministry of Education, Hangzhou 310058, China
[c] Zhejiang Provincial Key Laboratory of Organic Pollution Process and Control, Hangzhou 310058, China

ARTICLE INFO

Article history:
Received 2 August 2017
Received in revised form
3 October 2017
Accepted 9 October 2017

Keywords:
Biochar
Various biomass
Aromatic compounds
Adsorption
Correlation

ABSTRACT

Knowledge of adsorption behavior of organic contaminants on high heat temperature treated biochars is essential for application of biochars as adsorbents in wastewater treatment and soil remediation. In this study, isotherms of 25 aromatic compounds adsorption on biochars pyrolyzed at 700 °C from biomass including wood chips, rice straw, bamboo chips, cellulose, lignin and chitin were investigated to establish correlations between adsorption behavior and physicochemical properties of biochars. Isotherms were well fitted by Polanyi theory-based Dubinin-Ashtakhov (DA) model with three parameters, i.e., adsorption capacity (Q^0) and adsorption affinity (E and b). Besides the negative correlation of Q^0 with molecular maximum cross-sectional areas (σ) of organic compounds, positive correlations of Q^0 with total pore volume (V_{total}) and average diameter of micropore (D) of biochars were observed, indicating that adsorption by biochars is captured by the pore-filling mechanism with molecular sieving effect in biochar pores. Linear solvation energy relationships (LSERs) of adsorption affinity (E) with solvatochromic parameters of organic compounds (i. e., α_m and π^*) were established, suggesting that hydrophobic effect, π-π interaction and hydrogen-bonding interaction are the main forces responsible for adsorption. The regression coefficient (π_1) and intercept (C) of obtained LSERs are correlated with biochar H/C and R_{micro}, respectively, implying that biochars with higher aromaticity and more micropores have stronger π-π bonding potential and hydrophobic effect potential with aromatic molecule, respectively. However, hydrogen-bonding potential of biochars for organic molecules is not changed significantly with properties of biochars. A negative correlation of b with biochar H/C is also obtained. These correlations could be used to predict the adsorption behavior of organic compounds on high heat temperature treated biochars from various biomass for the application of biochars as sorbents and for the estimating of environmental risks of organic compounds in the present of biochars.

1. Introduction

Biochar is a type of charcoal produced by heating crop wastes, wood or other biomass in oxygen-limited condition, which has been extensively studied because of the potential applications in soil improvement, climate change mitigation, waste management and energy production (Lehmann, 2007; Chai et al., 2012; Yao et al., 2013). Studies have shown that the high heat temperature treated biochars produced at 600–700 °C have superior adsorption capability to organic contaminants because of their large surface area, fine microporosity and highly aromatic structure (Chen et al., 2008; Lattao et al., 2014; Srinivasan and Sarmah, 2015). Therefore, they were widely interested for their applications as potential sorbents in soil remediation and wastewater treatment (Pingnatello et al., 2006; Chen et al., 2008; Keiluweit et al., 2010; Lattao et al., 2014; Jin et al., 2016). They were also interested for their alternating on the fate, transport and bioavailability of organic contaminants in the environment by adsorption once they are released into the environment in their production, transportation, storage, disposal and especially use in soil improvement (Kwon and Pignatello, 2005; Beesley et al., 2010).

Correlations capable of predicting adsorption behaviors of organic compounds on high heat temperature treated biochars are

☆ This paper has been recommended for acceptance by Baoshan Xing.

* Corresponding author. Department of Environmental Science, Zhejiang University, Hangzhou 310058, China.
E-mail address: kyang@zju.edu.cn (K. Yang).

https://doi.org/10.1016/j.envpol.2017.10.035
0269-7491/

of great importance for their selected applications as potential sorbents and for the fate, transport and bioavailability of organic contaminants in the environment (Crittenden et al., 1999; Yang et al., 2016). In the previous study (Yang et al., 2016), we observed that isotherms of 25 aromatic compounds, including polycyclic aromatic hydrocarbons (PAHs), nitrobezenes, phenols, and anilines, on a bamboo biochar (Ba700) produced from bamboo chips at 700 °C were fitted well with the Polanyi-theory based Dubinin-Ashtakhov (DA) model. A negative relationship of DA model fitted Q^0 parameter (adsorption capacity) of organic compounds with their molecular cross-sectional areas (σ) were established, indicating that adsorption is captured by the pore filling mechanism. A liner solvation energy relationship (LSER) of DA model fitted E parameter (adsorption affinity) of organic compounds with their solvatochromic parameters (i.e., polarity/polarizability parameter π^* and hydrogen-bonding donor parameter α_m in Table S1) were also established, indicating that adsorption on the biochar is derived from the hydrophobic effects of organic compounds and the forming of π-π EDA and hydrogen bonding interactions of organic molecules with biochar surface sites. These correlations would be useful for quantitative estimating the adsorption of organic compounds on Ba700 from their commonly physiochemical properties including π^*, α_m and σ. However, whether these correlations established for Ba700 could be applicable for biochar produced from other biomass is unclear yet and need to be examined.

Besides the physiochemical properties of organic compounds, the structural and surface properties such as surface area, pore volume, pore size, surface oxygen-containing groups and aromaticity of biochars may also play crucial roles in the adsorption. For example, adsorption of simazine on biochar prepared by corn straw increased with the increasing of surface area (Zhang et al., 2011). Adsorption of biochar to organic contaminants was observed enhanced with the increasing of aromaticity of biochar, as increased aromatic rings can promote the π-π electron accepting ability of biochar to form stronger π-π bonds with aromatic molecules (Zhu et al., 2005; Chen and Chen, 2009; Lattao et al., 2014; Xie et al., 2014). Oxygen-containing groups on biochar surface can suppress adsorption of organic compounds, especially hydrophobic organic compounds, because oxygen-containing groups are hydrophilic and can form strong hydrogen-bonds with water molecules (Zhu et al., 2005). Biochars, made from different biomass such as plant tissue, crop residue, animal remains and biopolymers, are commonly with various structural and surface properties and thus having various adsorption for organic compounds (Fernandes et al., 2003; James et al., 2005; Nguyen et al., 2007; Kearns et al., 2014; Mandal et al., 2017). Therefore, it is critical to examine the adsorption on high heat temperature treated biochars produced from various biomass and to establish the correlations of adsorption capacity and affinity with structural and surface properties of biochars, for predicting adsorption behaviors of organic compounds on biochars and for exploring the underlying mechanisms.

In this study, adsorption of 25 aromatic compounds, the same chemicals (i.e., PAHs, phenols, anilines and nitrobenzenes) investigated for Ba700 in our previous study (Yang et al., 2016), on 5 biochars produced from different biomass including wood chips, rice straw, cellulose, lignin and chitin at 700 °C, were investigated by isotherm fitted using DA model to examine whether the correlations established for Ba700 (Yang et al., 2016) are applicable for biochar produced from other biomass. Moreover, based on the observed negative relationships of DA model fitted Q^0 with σ and the LSERs of DA model fitted E with solvatochromic parameters (i.e., π^* and α_m) of aromatic compounds on these 5 biochars in this study and the relationships on Ba700 reported in our previous study (Yang et al., 2016), the correlations capable of predicting adsorption were established. 25 organic compounds (i.e., PAHs, phenols, anilines and nitrobenzenes) were employed in this study, because they have significant difference in functional groups, solubility, melting points, solvatochromic parameters (i.e., $V_I/100$, π^*, α_m and β_m) and molecule size (Table S1). For example, the solubility is in a range from 0.135 mg/L to 80190 mg/L, varied in 7 orders of magnitude. In previous studies (Yang et al., 2008, 2016; Wu et al., 2016), we have gotten expected correlations with significance of statistical analysis using these 25 chemicals. These compounds are widely found in the effluents from dyestuffs, pesticides, petrochemicals, pharmaceuticals and other industries (Castilla, 2004; Laszlo et al., 2007; Zhang et al., 2007), which brought serious environmental pollution and risks for human's health and safety and have been listed as priority pollutants by US Environmental Protection Agencies (Castilla, 2004; Laszlo et al., 2007; Zhang et al., 2007). The biomass investigated in this study such as wood chips, bamboo chips and rice straw are ubiquitous in the environment and frequently-used plant biomass and crop residue. Lignin and cellulose were the vital components of plants. Chitin, widely exists in crab and shrimp shells, is the second most abundant polysaccharide after cellulose (Wang and Xing, 2007).

2. Materials and methods

2.1. Biochars and chemicals

Wood chips and rice straw were collected from Zhejiang, China. Cellulose, lignin (dealkaline) and chitin were purchased from J&K Scientific, Tokyo Chemical Industry and Aladdin Reagent Corporation, respectively. Biochars were prepared by heated biomass under oxygen-limited conditions in a muffle furnace at 700 °C for 6 h, as was described in detail in our previous study (Yang et al., 2016). The biochars prepared from wood chips, rice straw, cellulose, lignin and chitin were labeled as W700, S700, Ce700, Li700 and Ch700, respectively.

Twenty five aromatic chemicals, including 3 PAHs, 8 phenols, 7 anilines, 7 nitrobenzenes, the same chemicals used in our previous study (Yang et al., 2016) were employed in this study. Selected properties of these chemicals, including purity, water solubility (C_s), density (ρ), melting points (MP), cross-sectional areas (σ) and Kamlet-Taft solvatochromic parameters, including polarity/polarizability parameter (π^*), intrinsic molar volume (V_1), hydrogen-bonding acceptor parameter (β_m) and hydrogen-bonding donor parameter (α_m), are listed in Table S1 (Yang et al., 2008, 2016).

2.2. Characterization of biochars

N_2 sorption-desorption isotherms of biochars at 77 K were determined by a physisorption analyzer (Quantachrome, AUTOSORB AS-1) to calculate the surface area, pore volume and pore size of biochars. Specific surface area (SA) was calculated by multipoint Brunaer-Emmett-Teller (BET) method in the relative pressure (p/p_0) region of 0.05–0.3. Micropore surface area (A_{micro}) was calculated by t-plot method. Total pore volume (V_{total}) was estimated at p/p_0 of about 0.99. The Density Functional Theory (DFT) method (El-Merraoui et al., 2000) was employed to calculate micropore volume (V_{micro}). Average diameter of micropore (D, nm) was calculated by ratio of a quadruple micropore volume to surface area (Gregg and Sing, 1982). C, H and N contents of biochars were detected using a elemental analyzer (Thermo Finningan, Flash EA 1112 CHN). Ash content was measured by heating biochars at 800 °C for 1 h,