Available online at www.sciencedirect.com

ScienceDirect

Journal of Environmental Sciences 2013, 25(7) 1368–1378

JOURNAL OF
ENVIRONMENTAL
SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Role of sorbent surface functionalities and microporosity in 2,2′,4,4′-tetrabromodiphenyl ether sorption onto biochars

Jia Xin, Ruilong Liu, Hubo Fan, Meilan Wang,
Miao Li, Xiang Liu*

School of Environment, Tsinghua University, Beijing 100084, China. E-mail: xinj08@mails.tsinghua.edu.cn

Received 12 November 2012; revised 07 January 2013; accepted 24 January 2013

Abstract

The study provides insight into the combined effect of sorbent surface functionalities and microporosity on 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) sorption onto biochars. A series of biochars prepared under different conditions were used to test their sorption behaviors with BDE-47. The extents of sorption behaviors were parameterized in terms of the single-point adsorption equilibrium constant (K_{oc}) at three equilibrium concentration (C_e) levels ($0.001S_w$ (solubility), $0.005S_w$, and $0.05S_w$) which was determined using the Freundlich model. To elucidate the concentration-dependent dominant mechanisms for BDE-47 sorption onto biochars, K_{oc} was correlated with four major parameters using multiple parameter linear analysis accompanied with significance testing. The results indicated that at low concentration ($C_e = 0.001S_w$), the surface microporosity term, which represented a pore-filling mechanism, contributed significantly to this relationship, while as concentration was increased to higher levels, surface functionality related to surface adsorption began to take the dominant role, which was further confirmed by the results of Polanyi-based modeling. Given the above results, a dual mode model based on Dubinin-Radushkevich and de Boer-Zwikker equations was adopted to quantitatively assess the changes of significance of surface adsorption as well as that of pore filling with sorption process development. In addition, UV spectra of four typical aromatic compounds which represented the key structural fragments of biochars before and after interactions with BDE-47 were analyzed to determine the active functional groups and supply complementary evidence for the dominant interaction force for surface adsorption, based on which π–π electron-donor-acceptor interaction was proposed to contribute greatly to surface adsorption.

Key words: biochar; polybrominated diphenyl ethers (PBDEs); sorption; surface functionality; microporosity

DOI: 10.1016/S1001-0742(12)60222-8

Introduction

Polybrominated diphenyl ethers (PBDEs) are commonly used in industries due to their fire retarding properties, including in electrical appliances such as television and computers, building materials, and textiles (Alaee et al., 2003). They are a particularly problematic group of pollutants, not only because of their high level of toxicity at low concentrations but also because of their persistence in the environment and their tendency to bioaccumulation.

Recently, PBDEs were detected at high concentrations in various environmental compartments, of which soil was the most important phase for their accumulation and re-emission. Considerably high levels of PBDE congeners have been detected in soil samples from point source industrial areas, such as major e-waste recycling sites (Leung et al., 2007), PBDE production factory sites (Jin et al., 2011), and electronic appliance assembling sites (Zhang et al., 2009). In addition, PBDEs tend to be more and more widely detected in non-industrial areas, i.e., the Pearl River Delta (Guan et al., 2009), Yangtze River Delta (Duan et al., 2010), eastern urban area (Jiang et al., 2010) and central Loess Plateau (Meng et al., 2011), which may be caused by long-range transport and secondary emission. Thereby there is great urgency to control their further transport once PBDEs are released into the soil environment at high levels. Currently, "biochar," intentionally made by biomass pyrolysis, has received increasing attention as a possible soil amendment and a potential low-cost adsorbent to sequester contaminants and control pollutant migration (Zimmerman, 2010).

Like activated carbons, biochars are also produced by combustion processes (pyrolysis), but the source materials are generally limited to biological residues (e.g.,

---

* Corresponding author. E-mail: x.liu@tsinghua.edu.cn

wood, poultry litter, crop residues etc.) and not commonly activated or further treated before application to soils. Some biochars, unlike activated carbons, are not fully carbonized, and are therefore composed of different proportions of carbonized to amorphous organic matter and may react to contaminants in soils more like native soil organic matter (Beesley et al., 2011). Several previous studies have shown that the properties of biochars are strongly dependent on carbon precursor and formation conditions (Uchimiya et al., 2011; Wang et al., 2011), and that sorption properties are dependent not only on surface area and chemistry (Yu et al., 2010a; Zhang et al., 2011), but also on other properties, such as the char's content of authigenic organic phases (Yu et al., 2010b; Yan et al., 2011). As different mechanisms could impact the further fate and re-emission of sorbed contaminants after biochar amendments, to shed light on the involved mechanisms would pave a better way for post-remediation risk assessment and management.

Surface parameters and micropore structure are two classes of physicochemical properties that are recognized to exert an important influence on the extent of adsorption in biochar systems; they pertain to the coexisting interactions of surface adsorption and pore filling, respectively. The significance of surface adsorption or/and pore filling on hydrophobic organic compounds (HOCs) sorption has been pointed out in previous literature respectively (Zhu et al., 2005; Zhu and Pignatello, 2005a, 2005b; Ji et al., 2009). However, these previous works alluded to a single dominant sorption mechanism with little consideration given to the heterogeneous sorption development steps under specific conditions, so inconsistent and even contradictory conclusions have often been drawn about the contribution mode of simultaneously or separately involved surface adsorption and pore-filling mechanisms (Yang et al., 2006; Wang and Xing, 2007), which has created difficulties in clearly understanding the particular mechanism of interest and executing efficient related risk assessment.

In this study, batch sorption experiments were adopted to test the sorption behaviors of 12 biochars prepared from the same corn stalk at four pyrolytic temperatures (300°C, 400°C, 500°C, 600°C) with three different pyrolyzing periods (2, 4, 6 hr). Gradients of major physicochemical properties (such as O/C ratio, aromaticity, hydrophobicity and specific surface area (SSA)) were available among the prepared biochars. One typical PBDE congener, 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), which is included in the persistent organic pollutants (POPs) list and frequently detected in the natural environment at high concentration levels, was selected as the model PBDE to explore its interaction with the tested biochars. In order to attain deep insight into the coexisting interaction mechanisms of surface adsorption and pore filling, which depend on the sorption development process, the single-point sorption coefficient K_{oc} at three concentration levels (C_{e} (equilibrium concentration) = $0.001S_{\mathrm{w}}$ (solubility), $C_{\mathrm{e}} = 0.005S_{\mathrm{w}}$, $C_{\mathrm{e}} = 0.05S_{\mathrm{w}}$) was respectively correlated with key physicochemical properties that were proposed to impact the sorption process using multiple linear regression analysis to determine the key molecular describer, accompanied with significance testing. Based on this analysis, a dual-mode model based on Dubinin-Radushkevich (DR) and de Boer-Zwikker equations was adopted to quantitatively assess the significance of surface adsorption as well as that of pore filling. In addition, according to the selected molecular describer for surface adsorption, the ultraviolet (UV) spectra of model aromatic compounds with similar aromatic backbone structure but different substituents before and after interaction with BDE-47 were obtained to determine the active sorption sites and functional group-related mechanism for surface adsorption.

1 Materials and methods

1.1 Chemicals

BDE-47 was purchased from Aldrich Chemical Co. Inc. (Milwaukee, USA) with a purity > 98%. BDE-47 has a $\log K_{\mathrm{ow}}$ of 6.39, and solubility (S_{w}) of 94.7 μg/L. Stock solutions were prepared in methanol. Methanol and hexane were of high performance liquid chromatography (HPLC) grade (J. T. Baker, USA). All other chemicals ($CaCl_2$, NaN_3, HCl) were of analytical grade (Sinopharm Chemical Reagent Co., Ltd., China).

1.2 Preparation of biochars

Corn stalks (CS) were obtained from farmlands of the Daxing districts in Beijing and were used as received without pretreatments. Corn stalks were pyrolyzed at 300°C, 400°C, 500°C, and 600°C for 2, 4, 6 hr respectively under 1600 mL/min nitrogen flow rate using a box furnace (22 L void volume) with retort (Lindberg, Type 51662-HR, Watertown, WI, USA). The resulting biochars (CS300-2hr, CS400-2hr, CS500-2hr, CS600-2hr, CS300-4hr, CS400-4hr, CS500-4hr, CS600-4hr, CS300-6hr, CS400-6hr, CS500-6hr, CS600-6hr) were allowed to cool to room temperature overnight in the retort under 1600 mL/min nitrogen flow rate.

1.3 Characterization of biochar

Surface areas were measured in duplicate by nitrogen adsorption isotherms at 77 K using a NOVA 2000 surface area analyzer (Quantachrome, Boynton Beach, FL, USA). SSA was determined by the single-point method from adsorption isotherms with P/P_0 at 30%. Elemental composition (CHO) was determined by dry combustion using a Perkin-Elmer 2400 Series II CHNS/O Analyzer (Perkin-Elmer, Shelton, CT, USA).

To obtain information on surface functionalities, In-