Bioresource Technology 118 (2012) 120–127

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Polar and aliphatic domains regulate sorption of phthalic acid esters (PAEs) to biochars

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HIGHLIGHTS

- ▶ Sorption of PAEs by plant biomass-derived biochars was determined.
- ▶ Low-HTT biochars exhibited the high sorption of PAEs.
- ▶ The O and N groups jointly account for high sorption of PAEs for low-HTT biochars.
- ▶ Grass chars displayed higher PAEs sorption than wood chars.

ARTICLE INFO

Article history:
Received 23 March 2012
Received in revised form 1 May 2012
Accepted 4 May 2012
Available online 11 May 2012

Keywords:
Biochar
Black carbon
Phthalate esters (PAEs)
Sorption
Electron donor–acceptor (EDA)

ABSTRACT

Molecular variations among different biochar categories translate into differences in their ability to function as sorbents to three phthalic acid esters (PAEs) representing a gradient in hydrophobicity. The sorption capacity (K_{OC}) for all three PAEs was the greatest for amorphous biochars (heat treatment temperature HTT = 400 °C), followed by biochars produced at 300 °C, and was best explained by the hydrophobicity of the sorbate. Greater alkyl C content and higher polarity of grass chars versus wood chars prepared at similar temperatures explained both (a) the difference in sorbent strength between feedstocks and (b) the maximum in sorbent strength at relatively low HTTs (300–400 °C). Hydrophobic partitioning into 'soft' alkyl carbon and specific H-bonding involving char-bound O and N groups jointly account for high affinities of PAEs for low-HTT biochars. The results highlight the influence of feedstocks and HTTs on PAEs sorption strength and mechanism.

1. Introduction

It is widely accepted that adsorption limits the biodegradation of organic contaminants (including pesticides) by decreasing their aqueous concentrations and reducing their accessibility to enzymes and microorganisms in soils and sediments (Cornelissen et al., 2005; Chefetz and Xing, 2009). Thermally altered organic matter (including materials such as black carbon (BC), char, charcoal and biochar) is long known as a strong sorbent for organic contaminants, thus reducing their bioavailability in soils and sediments. Physical and chemical properties of thermally altered organic materials depend on the composition of the starting material and on the amount of thermal energy applied (heat treatment temperature, HTT) during the charring process. This fact asks for the question how the resulting sorptive efficacy of char-based sorbents may be predicted from the conditions of thermal treatment, or, in more practical terms, what the ideal treatment conditions are to produce a char designed for the adsorption of a specific compound. Past investigations (Bourke et al., 2007; Keiluweit et al., 2010) allow us to constrain a molecular model for chars manufactured at given HTTs. In this model chars are classified into molecular categories characterized by the relative contributions of (a) torrified plant material; (b) a 'soft', amorphous, flexible phase and (c) turbostratic crystallites of rigidly stacked, 'glassy' graphene sheets. The resulting sorbent properties can be derived from an established model of natural organic matter (Xing and Pignatello, 1997) which conceptualizes natural organic matter (NOM) as a heterogeneous mixture consisting of two distinct sorption domains. The domains are characterized as soft and condensed carbon, respectively, and the condensed carbon domain in NOM is increasingly understood to result from the ubiquitous admixture of BC to soils and sediments (Accardi-Dey and Gschwend, 2002; Kleber and Johnson, 2010). Recently, the concept of the two different sorption domains was adopted for the sorption of hydrophobic organic contaminants (HOCs) to biochars. Chen et al. (2008a) suggested that sorption

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0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2012.05.008