Sorption mechanisms of chlorinated hydrocarbons on biochar produced from different feedstocks: Conclusions from single- and bi-solute experiments

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HIGHLIGHTS

- Sorption of chlorinated hydrocarbons is strongly feedstock dependent.
- Sorption is comprised of partitioning and pore-filling.
- Size exclusion hinders PCE sorption in biochars with small micropores.
- Competition is stronger in microporous chars prepared from plant-based feedstocks.
- Competitive effects in microporous sorbents are concentration dependent.

GRAPHICAL ABSTRACT
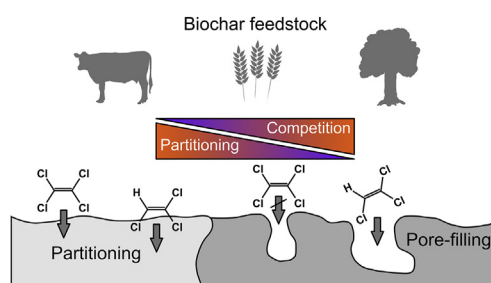
ABSTRACT

Biochar is increasingly deemed a potential sorbent for contaminants in soil and water remediation. We tested three biochars from different feedstocks (cattle manure, grain husk, and wood chips) produced at relatively low pyrolysis temperature (450 °C), for their sorption behavior towards trichloroethylene (TCE) and tetrachloroethylene (PCE) in single- and bi-solute systems. In single-solute experiments, all biochars show stronger sorption for TCE (about 50% based on solubility-normalized Freundlich coefficients). The lower sorption of PCE is attributed to steric effects, e.g. size exclusion in small micropores and specific interactions. Plant-derived, carbon-rich biochars with high specific surface area and microporosity predominantly sorb via pore-filling, as also observed in activated carbon. Biochar produced from manure, with higher ash content and polarity, and smaller total pore volume (PV_{tot}), shows significant contribution of partitioning. These findings also apply to bi-solute systems. TCE and PCE show different competition behavior depending on biochar properties. Plant-based biochars are pore-filling-dominated and show strong competition. However, competition behavior in microporous biochars depends on the concentration range. Manure biochar with high polarity and low PV_{tot} shows significant partitioning and therefore less competition. Compared to the plant-based chars competition in manure biochar is not concentration-dependent. These results indicate that biochars with a large fraction of non-carbonized phase facilitate non-competitive sorption and might be a valuable sorbent in mixed contaminant systems.

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1. Introduction

The immobilization of contaminants by adsorption is one of the most commonly applied techniques in soil and water remediation. In recent years, biochars have attracted attention as a potential sorbent for contaminants (Beesley et al., 2011; Ahmad et al., 2014b; Tan et al., 2015; Xie et al., 2015; Kumar et al., 2016), especially in brownfield restoration. Biochar is defined as a carbon-rich material obtained from pyrolysis of organic material such as plant residues or organic waste. It is often used in agriculture to enhance soil fertility, but also gained interest for the possibility to mitigate atmospheric CO_2 (Lehmann and Joseph, 2009). Numerous studies have demonstrated that biochar can sorb a wide range of organic contaminants, where most studies focused on the pyrolysis temperature as the main factor controlling biochar properties and sorption behavior. Due to the heterogeneous nature of biochar, sorption mechanisms are complex and often follow a combined partitioning-adsorption process (Chen et al., 2008, 2017; Chen and Chen, 2009; Chiou et al., 2015). Adsorption mainly takes place in the well carbonized, aromatic structure, whereas partitioning can occur in the non-carbonized phase (Chun et al., 2004). Depending on feedstock and pyrolysis conditions, biochars can contain a significant fraction of this not fully carbonized portion (Mohan et al., 2014).

Chlorinated hydrocarbons such as trichloroethylene (TCE) and tetrachloroethylene (PCE) are among the most detected contaminants in soil and groundwater (e.g. Damgaard et al., 2013). They were often used for metal degreasing, in dry cleaning, the textile industry, and in the production of chemicals (ATSDR, 2014; Matteucci et al., 2015; ATSDR, 2016). As TCE and PCE have similar physical-chemical properties and applications, they are often found together in contaminated sites.

Several studies investigated TCE sorption on biochars derived from different feedstocks and produced at varying pyrolysis temperatures. Ahmad and colleagues investigated buffalo-weed, soybean stover, and pine needle biochars and could show that sorption is positively correlated with surface area, hydrophobicity, and pore volume, which can be influenced by the pyrolysis temperature (Ahmad et al., 2012, 2013a, 2013b, 2014a). Han et al. (2017) discussed the differences between sorption with respect to biochar feedstock and directly compared TCE sorption to other chlorinated compounds. However, the aspect of partitioning and pore-filling, and associated effects, e.g. size exclusion, has received little attention for chlorinated hydrocarbons.

Many studies reported sorption of organic contaminants in bi-solute systems. Diverse effects were found, ranging from strong competition (e.g. Schaefer et al., 2000; Sander and Pignatello, 2005; Wang et al., 2006; Zheng et al., 2010; Jung et al., 2015; Wang et al., 2016a) to enhanced sorption in the presence of a co-solvent (Chen et al., 2012). Wu et al. (2017) proposed that competition of two pharmaceuticals is weaker in a low-temperature, partitioning-dominated biochar than in a biochar produced at higher temperature from the same material. However, the effect of biochar feedstock on sorption in bi-solute systems has received little attention. Also, most studies focus on isotherm-effects for the primary solute while adding the competing compound at a fixed concentration. Therefore, information on concentration-dependent effects in bi-solute systems are scarce.

In this study, we aim to (1) study the effects of different biochar feedstocks on the sorption of TCE and PCE, (2) explore competitive and concentration-dependent effects in bi-solute experiments, and (3) determine how sorbent properties influence partitioning and adsorption in both systems. To achieve this, one activated carbon (AC) and three biochars from different feedstocks, but produced at the same temperature, were selected.

2. Materials and methods

2.1. Sorbent characterization

Three biochars were derived from different feedstock materials: Cattle manure (BC-CM), grain husk (BC-GH), and wood ships (BC-WC). They were produced at a pyrolysis temperature of 450 °C to exclusively examine the effects of the feedstock material. BC-CM was produced at the Volcani Center (Israel). BC-GH and BC-WC were obtained from Sonnenerde (Austria). One commercially available powdered activated carbon (AC; Aquasorb G9, Jacobi Carbons, Germany) was included as a fully-carbonized, microporous reference. Sorbents were dried (105 °C) and biochars were ground to a fine powder with a vibratory disk mill (Siebtechnik, Germany) before further analysis.

Ash content was determined gravimetrically after heating (750 °C, 6 h) in a muffle furnace (triplicate determination) (ASTM D 1762-84, 2013). Elemental composition (C, H, N, and S) was determined in duplicates by combustion (1000 °C) in an oxygen stream using an elemental analyzer (vario EL cube, Elementar, Germany; analysis performed by Zeta Partikelanalytik, Mainz, Germany). The oxygen content was calculated by mass balance: O = 100 - (C + H + N + S + ash) in weight-% (similar to Kah et al., 2016). Organic carbon content (C_{Org}) was measured with a carbon analyzer equipped with an IR detector (LiquiTOC II, Elementar, Germany).

Specific surface area (SSA), total pore volume (PV_{tot}), micropore volume (PV_{mic}), and pore size distribution were determined by argon sorption using a Micromeritics 3Flex sorption analyzer (Micromeritics Instrument Co., Norcross, USA). Argon (at 87 K) was chosen as the adsorbate, because it is non-polar and therefore does not suffer from polar interactions with the surface functional groups of the microporous sample material (Thommes et al., 2015). Details on data evaluation are available in the Supplementary Material.

2.2. Sorption experiments

Sorption experiments were conducted in 50 mL headspace vials with Teflon-lined crimp top caps in a 0.01 M $NaClO_4$ aqueous solution (prepared from $NaClO_4$ monohydrate, CAS 7791-07-3, Merck Millipore, Germany) to maintain a constant ionic strength. Appropriate amounts of sorbent (0.4 mg—0.5 g) were added to the vials to achieve a decrease in solute concentrations of 20—90%. Samples >15 mg were weighed on an analytical balance (Ohaus Explorer Pro; precision ± 0.1 mg) directly in the headspace vials. Amounts <15 mg were weighed in tin boats on a micro balance (Sartorius Micro M 500 P; precision ± 0.01 mg) and transferred to the reaction vials. Both solutes were spiked dissolved in methanol. The added volume never exceeded 0.5% to exclude co-solvent effects (Nkedi-Kizza et al., 1987). All experiments were run in triplicate, accompanied with blank and sorbent-free control samples.

Vials were placed on a horizontal shaker and agitated for 7 days in the dark under ambient conditions (20 °C ± 1). Preliminary kinetic experiments had shown that this period is sufficient to reach sorption equilibrium (data not shown). Aqueous phase concentrations were determined using static headspace sampling with gas chromatographic separation, and flame ionization (FID) or electron capture (ECD) detection. More details on the analytical protocols are given in the Supplementary Material.

2.3. Data analysis

All sorption data were fitted to the Freundlich isotherm model (Freundlich, 1909),