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Effect of biochar particle size on hydrophobic organic compound sorption kinetics: Applicability of using representative size



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Phenanthrene sorption rate strongly depends on biochar particle size.
 The sorption kinetics is well described
- by the intraparticle diffusion model.
- Harmonic intensity averaged radius (*R*_z) is used as a representative biochar radius.
- *R*_z describes the dependence of sorption kinetics on biochar particle size.



Time * Rz is representative particle radius using weighted harmonic mean formula

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ABSTRACT

Particle size of biochar may strongly affect the kinetics of hydrophobic organic compound (HOC) sorption. However, challenges exist in characterizing the effect of biochar particle size on the sorption kinetics because of the wide size range of biochar. The present study suggests a novel method to determine a representative value that can be used to show the dependence of HOC sorption kinetics to biochar particle size on the basis of an intra-particle diffusion model. Biochars derived from three different feedstocks are ground and sieved to obtain three daughter products each having different size distributions. Phenanthrene sorption kinetics to the biochars are well described by the intra-particle diffusion model with significantly greater sorption rates observed for finer grained biochars. The time to reach 95% of equilibrium for phenanthrene sorption to biochar is reduced from 4.6– 17.9 days for the original biochars to <1–4.6 days for the powdered biochars with <125 μ m in size. A moderate linear correlation is found between the inverse square of the representative biochar particle radius obtained using particle size distribution analysis and the apparent phenanthrene sorption rates determined by the sorption kinetics experiments and normalized to account for the variation of the sorption rate-determining factors other than the biochar particle radius. The results suggest that the representative biochar particle radius reasonably describes the dependence of HOC sorption rates on biochar particle size.

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1. Introduction

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Biochar, produced via pyrolysis of biomass, is a promising sorbent to treat water, soil, and sediment impacted by a wide range of

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contaminants (Ahmad et al., 2014; Inyang et al., 2016; Mohan et al., 2014; Rajapaksha et al., 2015). There is a growing body of literature demonstrating the potential of biochar to remove pollutants from water and immobilize soil and sediment pollutants (Ahmad et al., 2016; Lehmann et al., 2015; Rizwan et al., 2016; Ok et al., 2015). Generally, benefits of using biochar in environmental applications include cost-effectiveness, climate change mitigation, and contribution to sustainable waste management (Ahmad et al., 2014; Hussain et al., 2017; Lehmann et al., 2006). For example, substituting activated carbon with biochar for hydrophobic organic compound (HOC) treatment can substantially reduce the carbon footprint of the process (Choi et al., 2016a).

The HOC sorption on biochar depends on various factors. The affinity to HOCs depends on surface area, pore size, porosity, and the degree of carbon condensation of biochar (Sun et al., 2013; Zhang et al., 2014). Biochar feedstock is one of the major factors that affect such physico-chemical characteristics. Biochars derived from different feedstock were shown to have large variation in surface area, pore size, porosity, and O/C and H/C ratios (Ahmad et al., 2014; Hale and Werner, 2010). Biochar treated with high pyrolysis temperature has higher carbon contents, which is favorable for HOC sorption (Ahmad et al., 2013b, 2012; Chen and Yuan, 2011). The development of micropores at higher pyrolysis temperature increases biochar surface area, which also improves the HOC sorption capacity (Downie et al., 2009).

While many studies evaluated the biochar sorption affinity to HOCs, less attention has been paid to the kinetics of HOC sorption on biochar (Ahmad et al., 2013a; Rajapaksha et al., 2015). For evaluating the performance of biochar as an HOC sorbent, the sorption rate may be an important characteristic that should be considered in addition to the sorption affinity. Understanding sorption kinetics is important for design and operation of many sorbent-based water treatment processes (Matoug et al., 2015). Sorption rate significantly influences the overall effectiveness of carbonaceous material to treat HOCs in a sediment or soil amendment (Werner et al., 2006). Previous studies have shown that particle size of porous, carbonaceous sorbents plays a major role for sorption kinetics of the sorbents (Choi et al., 2013a). For porous sorbents, most of the sorption sites are located in the intra-particle pores other than the external surface (Brusseau and Rao, 1989). Finer porous sorbent particles provide shorter intra-particle diffusion lengths for HOC sorption, which reduces the time required for equilibrium (Ahn et al., 2005). Therefore, knowledge on the effect of biochar particle size on HOC sorption kinetics is essential to predict the performance of biochar as a sorbent and tailor the biochar particle size for different environmental applications (Oleszczuk et al., 2016).

One of the challenges for characterizing the effect of biochar particle size on sorption kinetics is that biochar usually has a wide particle size range mainly due to the non-uniform size of the precursor materials (Rees et al., 2014; Shivaram et al., 2013). Therefore, it is difficult to represent the biochar particle size with a single value. Conventionally, a representative particle size for a granular material is often expressed as the particle diameter at 10%, 50%, or 90% of the cumulative particle size distribution (i.e., D₁₀, D₅₀, or D₉₀) (Blott and Pye, 2001). However, no studies to date have evaluated whether these representative particle sizes can accurately represent the relevant influence of biochar particle size on its sorption kinetics.

The goal of this study is to investigate the biochar particle size effect on HOC sorption kinetics and propose a method to determine a representative particle size that is relevant to the sorption kinetics. Three types of biochar produced from different feedstocks are processed further to obtain products with different size distributions. The sorption rates for the biochars with different size distributions are compared. A method to determine a representative biochar particle size from particle size distribution data is suggested based on theoretical interpretation of an HOC sorption model, and the validity of the method is examined using experimental data.

2. Materials and methods

2.1. Materials

Organic solvents (hexane, acetone and methanol) in pesticide or HPLC grade were purchased from Fisher Scientific Co. (Hampton, NH). Low density polyethylene (PE) with a thickness of 51 µm was obtained from Brentwood Plastics (St. Louis, MO) and used as a passive sampling device. Phenanthrene (98% purity; Sigma Aldrich, St. Louis, MO), a member of polycyclic aromatic hydrocarbons (PAHs), was used as a model sorbate.

Three different types of biochars, all commercially available, were studied in this work. Two of them were provided by the Korea Biochar Research Center at Kangwon National University (Chuncheon, Korea). These biochars were produced at a pyrolysis temperature of 500 °C using rice husk and sewage sludge. The other type of biochar was obtained from Kyungdong Energy Co., Ltd. (Seoul, Korea), which was derived from wood chip pyrolyzed at 250 °C. The physico-chemical properties of the biochars are shown in Table 1. For proximate analysis, moisture, mobile matter, resident matter, and ash contents were determined using the procedure described in Ahmad et al. (2013b). For ultimate analysis, elemental compositions of ash- and moisture-free biochars were determined using an elemental analyzer (Thermo Finnigan LLC, San Jose, CA; EA2000 for carbon and EA1112 for oxygen). Pore size, specific surface area, porosity, and skeletal density were determined using a mercury intrusion porosimetry (Autopore IV 9520; Micrometrics Instrument Corp., Norcross, GA). Mercury intrusion porosimetry is widely applied to determine such characteristics simultaneously by tracking the intrusion of mercury, a non-wetting liquid, to intra-pore of a specimen at incremental external pressure (Giesche, 2006; Moura et al., 2005). Mercury intrusion porosimetry characterizes pores with openings from a few nanometers to a few hundred micrometers (mesopore and macropore range) (Giesche, 2006), which account for the majority of the biochar pore volume (Brewer et al., 2014). The nitrogen absorption with BET analysis provides information of pores in the <2 nm-50 nm range but not those in the macropore range (Brewer et al., 2014). It should be noted that, however, mercury intrusion porosimetry may underestimate the specific surface area as micropores often significantly contribute to the overall biochar surface area, and that measurement errors in specific surface area determination may be more significant compared to the BET analysis (Giesche, 2006).

2.2. Biochar processing and particle size distribution analysis

The biochars received were further processed to obtain particles with three different size ranges for each type. The biochars were gently ground by a mortar and pestle, and passed through sieves with 125 μ m openings to obtain particles with lower sizes than the corresponding sieve size. These biochars are referred to as 125BC. Similarly, the biochars passed through 250 μ m-size sieve are referred to as 250BC. The biochars without any grinding or sieving is referred to as Un-BC. The 250BC and 125BC samples were analyzed using the mercury intrusion porosimetry and the results are summarized in Table 1.

Particle size distribution analysis was conducted using stacked sieves with different opening sizes. For Un-BC, opening sizes of 4, 2, and 1 mm, and 500, 250, 150, and 75 μ m were used while those of 200, 150, and 75 μ m opening sizes were used for 250BC. For 125BC, 106, 75, and 63 μ m opening sizes were used. The mass fraction in each size range was measured after the sieve separation.

2.3. Sorption kinetics experiment

Passive sampling technique was used to monitor the progress of phenanthrene sorption during the biochar sorption kinetics experiment. Accurate measurement of aqueous phenanthrene concentration Download English Version:

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