Science of the Total Environment 578 (2017) 399–407

Contents lists available at ScienceDirect

Science of the Total Environment

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

The systematic characterization of nanoscale bamboo charcoal and its sorption on phenanthrene:A comparison with microscale

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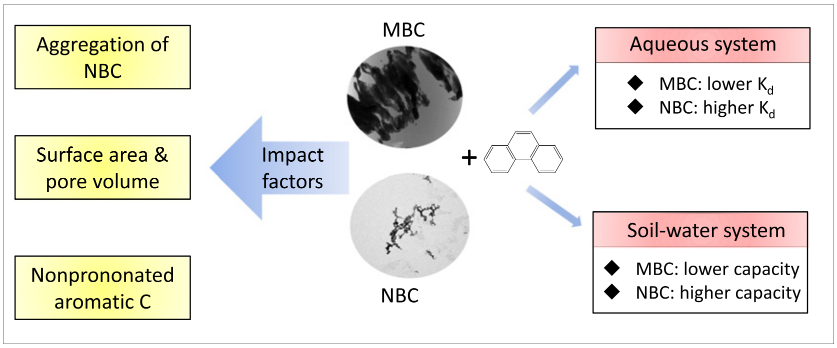
HIGHLIGHTS

- Physical and chemical properties of nanoscale bamboo charcoal were systematically investigated.
- Nanoscale bamboo charcoal was tested for phenanthrene sorption in aqueous and soil-water systems.
- Nanoscale bamboo charcoal had high ability for phenanthrene sorption in soil-water system, even at a low addition rate of 0.2% in soils.
- Nanoscale bamboo charcoal would be more competitive than some biochars in aqueous and soil-water systems.
- This finding increases our knowledge of nanoscale bamboo charcoal for organic pollutants remediation in soil.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 September 2016
Received in revised form 25 October 2016
Accepted 25 October 2016
Available online 8 November 2016

Keywords:
Bamboo charcoal
Phenanthrene
Sorption
Nanoscale

ABSTRACT

This study investigated the characteristics of nanoscale bamboo charcoal (NBC), and made a comparison with microscale bamboo charcoal (MBC) on how they impact on the sorption abilities of different soils. The two charcoals contained similar elemental contents (e.g., high C, low H and low N) and various functional groups on their surfaces (e.g., aromatic structure, carboxyl, and hydroxyl). However, NBC had a larger total pore volume than that of MBC and was more likely to generate multi-layer sorption of phenanthrene. Controlled by van der Waals forces and electrostatic forces, NBC formed meso-and macropores (intra-particle porosity) and a more intricate pore structure. The performance of NBC in aqueous and soil-water systems was conspicuous and impressing. In aqueous system, by virtue of its larger pore volume, surface area and nonprotonated aromatic carbon, the K_d (sorption coefficient) of NBC reached up to 1.24×10^6, almost 10 times higher than that of MBC. In soil-water systems, although it could aggregate and react with compounds in soil, the performance of NBC was not weakened by the complicated soil properties, and was still more capable of phenanthrene sorption than MBC, even at an extremely low addition rate 0.2% in soils. Additionally, in comparison with some other common biochars, NBC still showed a promising capacity for phenanthrene sorption in two systems. This finding increases our knowledge of NBC for the remediation of organic pollutants in soil and indicates that the addition rate of charcoals in soils could be reduced by lessening the particle size. Therefore, NBC provides a new possibility for soil pollutant remediation and deserves further research.

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http://dx.doi.org/10.1016/j.scitotenv.2016.10.196
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1. Introduction

With the rapid development of the fossil fuel industry, polycyclic aromatic hydrocarbon (PAH) accumulation poses a serious threat to human health. Owing to their low aqueous solubility, high binding affinity with soil organic matter, and high chemical stability, PAHs tend to biologically accumulate in the food chain (Yebra-Pimentel et al. 2015). Therefore, PAHs exhibit various properties, including volatilization, biomagnification, photo-oxidation, chemical oxidation and biodegradation (Mahanty et al. 2011; Yebra-Pimentel et al. 2015). Nowadays, researchers have invented various chemical, physical and biological methods to decontaminate soil (Wilcke 2000). As a typical model PAH pollutant, phenanthrene has been removed from soil by many novel and creative methods, such as ultrasound, soil washing (Song et al., 2012), an electrokinetic-Fenton method (Kim et al., 2006) and electro-kinetic remediation (Alcantara et al. 2008). Unfortunately, these existing methods have revealed some shortcomings, including laborious steps, expensive cost and a long time to do the analyses (Kim et al., 2006; Song et al., 2012; Alcantara et al. 2008). As a consequence, there is still a need to find a low-cost, efficient and convenient way to reduce or remove phenanthrene from soil.

Bamboo charcoals (BCs) are multifunctional materials pyrolyzed from bamboo under anaerobic conditions. During pyrolysis, bamboo, a type of plant biomass, is converted to stable charcoal. Due to its feedstock's high availability, porous structure and large surface area, BCs have been widely applied to help environment protection and as architectural decorations (Li et al. 2015). Many studies have reported that BCs have excellent abilities to absorb heavy metals (Wang et al. 2010a; Liu et al. 2012), organic pollutants (Ma et al. 2010), dyes (Wang and Yan 2011a; Liao et al. 2012) and other substances (Asada et al. 2006; Liao et al. 2013). Also, BCs have exhibited a high ability to purify waters, soils and sediments contaminated by PAHs. For example, Yang et al. (2016) investigated the sorption isotherms of various aromatic compounds onto BCs (pyrolyzed at 700 °C) in aqueous systems and made a correlation analysis to quantitatively estimate sorption processes. Li et al. (2012) explored the influences of BC addition to composted sludge on soil quality and plant growth, and found that composted sludge amended with BCs resulted in a better improvement in plant growth and less negative effects on plant and soil. Some studies even directly utilized bamboo wood to remove PAHs from water, but the sorption performance was not good as expected (Chen et al. 2011; Xi and Chen, 2014). After the modification of de-sugaring, the capacity of bamboo wood increased a lot and the polarity of this sorbent was regarded as an important factor in sorption mechanisms (Xi and Chen, 2014). As research continues, the application of BCs is always seeking new breakthroughs. Cha et al. (2016) pointed out that the modification of BCs is a promising trend in future research. Consequently, BCs and modification product of BCs are carbonaceous materials with great potential in environmental remediation.

In recent decades, nanotechnology has undergone dramatic developments. Because of their remarkable properties (e.g., catalyst, magnetism, optical property), nanoparticles (NPs) have exhibited a great potential for environmental remediation (Pan and Xing 2010; Li et al. 2016). Pollutants can be adsorbed on the surfaces of NPs, sorbed into them, or blocked by aggregation of NPs (Christian et al. 2008). However, NPs, particularly those that are uncoated, readily aggregate, deposit on or are immobilized by soil particles, thus restricting their reactions with contaminants (O'Carroll et al. 2013). Hence, the stability of NPs is a decisive factor in their surface properties and application. At present, there are two major approaches to solve the problem of stability: (i) adding dispersants to develop stable suspensions and (ii) optimizing the surface of NPs with inert materials (e.g., silica, polymers and surfactants) (Li et al. 2016). Compared to the above complicated methods, finding a convenient approach or a suitable material is still urgently needed. Kumari et al. (2014) claimed that bamboo charcoal was relatively stable in soil, so properly combining nanotechnology and bamboo charcoals may be a good way to enhance their efficiency. Although there are some studies of pollutant sorption on black carbons related to particle size, this research commonly has two defects: (i) it is mainly focused at the micrometer (Zheng et al. 2010; Müller 2010), rather than at the nanoscale level and (ii) experiments using NPs have mainly focused on aqueous systems (Tan et al. 2016), rather than soil-water systems.

In this study, phenanthrene was chosen as a representative PAH, and its sorption by BCs-amended soils and BCs in different systems was further explored. The major objectives were: (i) to systematically examine property variations between microscale bamboo charcoal (MBC) and nanoscale bamboo charcoal (NBC); (ii) to determine the sorption capacity of MBC and NBC in aqueous system; (iii) to investigate the performance of BCs in the soil-water system and the impact of the addition rate of BCs in soils. These results clearly illustrated the great sorption ability of NBC and also provided a solid foundation for further research.

2. Materials and methods

2.1. Sorbents and sorbates

The BCs used in this study were purchased from Shanghai HaiNuo Charcoal Co. Ltd. (Shanghai, China). The sizes of the BCs were: < 15 μm and < 100 nm, which corresponded to MBC and NBC, respectively.

Soils were sampled from Jilin (JL) and Hainan (HN) provinces. All samples were collected from the 0–15 cm depth. Sites were located in a Nature Reserve to minimize the impact of human activities. Before the experiments, each sample was air-dried and milled to pass through a 10 mesh sieve (for basic physicochemical properties analysis) and a 60 mesh sieve (for sorption experiments) separately.

Soils amended with BCs were prepared by thoroughly mixing the BCs and soils at different ratios. The percentages of BCs in the tested soils were 0.2%, 0.5% and 1.0% (*w*/w) (Wang et al. 2013).

All chemicals used were of analytical grade or above. Phenanthrene, with a purity of 98%, was purchased from Aldrich Chemical Co. The solubility of phenanthrene in water (S_W) is 1.18 mg L^{-1} and the octanol-water partition coefficient (Log K_{OW}) of phenanthrene is 4.46 (Zeng et al. 2014).

2.2. Characterization of soils and BCs

2.2.1. Characterization of soils

The soil properties are shown in Table S1, including USDA classification, pH, total organic carbon (TOC), mechanical composition, and cation exchange capacity (CEC). The analytical soil data in Table S1 were obtained by conducting measurements according to the National Standards of China (Lu 1999). Details can be found in Supplementary Materials. The two soils differed in their basic physical and chemical properties (Table S1). The TOC of the JL soil was 17.41 g kg^{-1}, three times higher than that of the HN soil (5.74 g kg^{-1}). The CEC of the JL soil was 26.18 cmol kg^{-1}, four times higher than that of the HN soil (6.08 cmol kg^{-1}).

2.2.2. Characterization of BCs

The BCs were characterized for physical and chemical properties. Elemental properties were measured with an EA1112 Elemental Analyzer (CE Instruments Ltd., Italy). Ash contents were measured by heating the samples in a muffle furnace at 750 °C for 4 h (Jin et al. 2014). Atomic ratios were calculated based on basic elemental contents. The pH values of the BCs were determined by a glass combination electrode (BCs/water ratio of 1:10 m:v). The pH_{PZC} (point of zero charge) values of the BCs were determined using the pH drift method with a pH meter (Peng et al. 2015). The zeta potential of NBC was measured with a Zetasizer Nano ZS90 (Malvern, U.K.). The physicochemical properties of MBC and NBC are shown in Table 1.

The surface areas (N_2-BET) and pore volumes of the BCs were determined from a physical sorption/desorption isotherm at 77 K using a