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Transport and retention of biochar nanoparticles in a paddy soil under environmentally-relevant solution chemistry conditions☆

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ABSTRACT

Land application of biochar has been increasingly recommended as a powerful strategy for carbon sequestration and soil remediation. However, the biochar particles, especially those in the nanoscale range, may migrate or carry the inherent contaminants along the soil profile, posing a potential risk to the groundwater. This study investigated the transport and retention of wood chip-derived biochar nanoparticles (NPs) in water-saturated columns packed with a paddy soil. The environmentally-relevant soil solution chemistry including ionic strength (0.10–50 mM), electrolyte type (NaCl and $CaCl_2$), and natural organic matter (0–10 mg L^{-1} humic acid) were tested to elucidate their effects on the biochar NPs transport. Higher mobility of biochar NPs was observed in the soil at lower ionic strengths, with $CaCl_2$ electrolyte being more effective than NaCl in decreasing biochar NPs transport. The retained biochar NPs in NaCl was re-entrained (~57.7%) upon lowering transient pore-water ionic strength, indicating that biochar NPs were reversibly retained in the secondary minimum. In contrast, negligible re-entrainment of biochar NPs occurred in $CaCl_2$ due to the primary minimum and/or particle aggregation. Humic acid increased the mobility of biochar NPs, likely due to enhanced electrosteric repulsive interactions. The transport behaviors of biochar NPs can be well interpreted by a two-site kinetic retention model that assumes reversible retention for one site, and irreversible retention for the other site. Our findings indicated that the transport of wood chip biochar NPs is significant in the paddy soil, highlighting the importance of understanding the mobility of biochar NPs in natural soils for accurately assessing their environmental impacts.

1. Introduction

Biochar is a pyrogenic carbon produced from bioenergy feedstocks or agricultural wastes in limited oxygen at relatively low temperatures (Lehmann, 2007). Recently, land application of biochar has been widely implemented for carbon sequestration, soil amendment, nutrient retention, and contaminant immobilization (Atkinson et al., 2010; Abit et al., 2014). The biochar particles applied in soils have a wide size range. Depending on the feedstock sources and pyrolysis temperature, the weight of the biochar nanoparticles (NPs) ranges from 1.6% to 2.6% of the total generated biochar particles (Wang et al., 2013a). Although the biochar NPs have a relatively smaller portion among the biochar populations compared to those of larger ones, these small biochar particles are reactive and will horizontally leach into surface water via runoff, drainage, or irrigation (Zhang et al., 2010; Guggenberger et al., 2008). The biochar NPs may likely migrate down along the soil profile via infiltration and enter the groundwater system, posing potential environmental risks because the pyrolyzed biochar could be intrinsically enrich in organic contaminants (PAHs and dioxins) (Hale et al., 2012; Oleszczuk et al., 2013). Furthermore, the biochar NPs that inherently exhibit high sorption affinities for a wide array of environmental contaminants (e.g., inorganic, organic, and pathogenic microorganism) (Cao et al., 2009; Chen et al., 2008; Hale et al., 2011), are likely to expedite the transport and wide dissemination of sorbed contaminants via ‘colloid-facilitated

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transport' (Fang et al., 2016). Therefore, a full understanding of the fate and transport of biochar NPs is critical to better optimize their benign use in agronomic and environmental advantages, but also to evaluate and minimize potential negative impacts of biochar NPs and biochar-facilitated transport of contaminants in the subsurface environments.

A few studies have been done to reveal the transport and retention of biochar particles including NPs in water-saturated porous media (Wang et al., 2013a, 2013b; Zhang et al., 2010). The findings indicate that the mobility of biochar particles depends on both the physicochemical properties of surrounding environmental conditions (e.g., ionic strength, pH, and natural organic matter) and the innate properties of biochar (particle size and pyrolysis temperature). For instance, Wang et al. (2013a). reported that the biochar NPs produced at lower pyrolysis temperatures exhibit higher mobility in saturated sand columns due to stronger Lewis acid-base repulsive interactions. Larger biochar micrometer particles transport less through sand columns than smaller NPs due, in part, to greater physical straining and surface charge heterogeneity among micrometer particle populations (Wang et al., 2013a). The authors also found the antagonistic interplay of humic acid and iron oxide grain-coating on the transport of biochar NPs (Wang et al., 2013b). In comparison, Zhang et al. (2010). found that the transport of biochar bulk particles (<75 μm) reduces with decreasing pH and increasing ionic strength. Please note that, however, all previously published studies focus solely on the transport of biochar particles in well-defined model porous media, i.e., cleaned quartz sand or iron oxide-coated sand grains; and the knowledge on the transport of biochar NPs in more realistic subsurface environments (i.e., natural soils) is fairly limited (Leifeld et al., 2007; Major et al., 2010).

Natural soils are highly complicated and heterogeneous in terms of their physicochemical and biological characteristics, and thus the actual transport behaviors of biochar NPs in natural soils would be distinct from those obtained in well-defined model porous media (Sun et al., 2015; Quevedo and Tufenkji, 2012; Zhang et al., 2012a). The variety of soil properties such as pH, pore-water ionic strength and cation type, surface roughness, particle size distribution, preferential flow pathway, surface chemical heterogeneity, and organic matter can play a role in the transport of biochar NPs, which is not captured by model porous media (Jaisi and Elimelech, 2009; Sagee et al., 2012; Wang et al., 2014a; Fang et al., 2009). Therefore, the transport of NPs in model porous media may be less applicable to predict the actual mobility of NPs in natural soil (Wang et al., 2010). Because the soil pore-water often includes different types of cations with varying concentrations, and NPs could be surface-modified with humic acid during transport, resulting in complex transport behaviors of NPs in natural soil (Jaisi and Elimelech, 2009; Sagee et al., 2012). However, to our knowledge, no studies have been done unraveling the mobility of biochar NPs in natural soils.

The objective of this study is to elucidate the transport and retention of biochar NPs in a natural paddy soil at environmentally-relevant solution chemistry including ionic strength, cation type, and humic acid concentrations. The mechanisms governing biochar NPs' transport and retention in the soil are interpreted using the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory in combination with colloid transport model that includes different retention rate coefficients for biochar NPs in the soil.

2. Materials and methods

2.1. Preparation of biochar NPs influent suspensions and porous soil media

The biochar was generated by pyrolyzing wood chip feedstocks under N_2-atmosphere at 500 °C with a heating rate of 20 °C min^{-1} and a holding time of 2 h. The rationale of employing the wood chip biochar is that the biochar is rich in carbon with very low content of minerals (Zhao et al., 2013), which could minimize the potential interferences of the biochar-inherent minerals with soil minerals. The biochar NPs used in the soil column transport experiments (described below) were prepared by grinding the biochar into powders using a ball grinder (QM-3SP04, China), and passing through a 200-mesh sieve. Physicochemical properties of the biochar NPs such as pH, particle size distribution, specific surface area, elemental compositions, etc. were determined (Table S1 in Supporting Information). The detailed procedures for characterizing these physicochemical properties are given in S1. Prior to the transport experiments, 200 mg L^{-1} biochar NPs influent suspensions were prepared by suspending 0.03 g biochar NPs into 150 mL solution containing different NaCl and $CaCl_2$ concentrations (1.0, 10, and 50 mM NaCl; 0.10, 0.50, and 1.0 mM $CaCl_2$; and 0, 5.0, and 10 mg L^{-1} humic acid (HA) in 1.0 mM NaCl and 0.10 mM $CaCl_2$, respectively). The 250 mg L^{-1} HA stock solution was prepared by introducing 62.5 mg of dry HA powder (Sigma Aldrich, Germany) into 250 mL deionized water (18.2 MΩ cm). A predetermined volume of HA stock solution was spiked into the biochar NPs influent suspension to generate the biochar NPs suspensions with the presence of 5.0 and 10 mg L^{-1} HA. The pH of biochar NPs influents was unbuffered but stable with the range between 7.41 and 7.60 (Table 1). Before initiating the column experiments, the biochar NPs influents were sonicated for 30 min.

A surface (0–20 cm) paddy soil sample was used as pore media that was collected from a farm field in the suburban of Changshu city, China. Prior to use, the collected soils were air-dried, crushed, and passed through sieves to obtain soil aggregates with sizes ranging from 600 to 710 μm (650-μm median grain size). This size fraction accounted for >80% of the total soil mass. Selected physicochemical properties of the soil aggregates were determined and the results are shown in Table S2.

The zeta potential and electrophoretic mobility of biochar NPs influents and soils at the desired solution chemistry were determined using the Zetasizer Nano-ZS analyzer (Malvern Instrument Inc., UK). The soil suspension was prepared by suspending a certain amount of soil into background solutions, followed by sonication for 30 min and filtration through a 0.45-μm filter. All measurements were run in triplicate, and the average values and standard deviations were reported (Table S3).

2.2. Column experiments

Biochar NPs transport experiments were conducted in glass chromatography columns (1.2-cm diameter × 6-cm length) that were wet-packed with the soil aggregates. The 80-μm nylon films (NY80, Merck Millipore Ltd.) were equipped at column ends. Detailed column packing procedures were described elsewhere (Chen et al., 2015). The porosity of packed columns was determined gravimetrically to be 0.49–0.54. Once packed, the soil columns were slowly preconditioned by pumping a 20 mM $CaCl_2$ solution at continuous increasing flow rates for 6.5 h to stabilize the soil colloids using a peristaltic pump (BT100-2J, Baoding Longer Precision Pump Co., Ltd., China). Afterwards, soil columns were saturated with desired electrolyte solution for another 6.5 h. The flow rate was then increased to the targeted one of 0.25 mL min^{-1} (Darcy velocity = 0.221 cm min^{-1}) which was close to the range of typical infiltration rate regime (e.g., 0.043–0.162 cm min^{-1}) (Martin and Moody, 2001), and this process was maintained for at least 4 h.

After the completion of soil colloid stabilization step, 4 pore volumes (PVs) of 1 mM NaBr conservative tracer were injected into the column to obtain the average pore-water velocity and dispersivity by fitting NaBr breakthrough curves (BTCs) (Fig. S1) using