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Application of biochar in the field has received considerable attention in recent years, but there is still little known about the fate and transport of biochar colloids (BCs) in the subsurface. Natural organic matter (NOM), which mainly consists of humic substance (HS) and proteins, is ubiquitous in the natural environment and its dissolved fraction is active and mobile. In this study, the transport of BCs in saturated porous media has been examined in the presence of two HS (humic and fulvic acids) and two proteins. Bull serum albumin (BSA) and Cytochrome c (Cyt) were selected to present the negatively and positively charged protein, respectively. At low and high salt concentration and different pH conditions, the transport of BCs was strongly promoted by HS. HS significantly increased the mobility of BCs in porous media under both low and high salt conditions due to the enhanced electrostatic repulsion and modification of surface roughness and charge heterogeneity. While BC mobility in porous media was suppressed by both BSA and Cyt in the low salt solution, the presence of BSA largely promoted and Cyt slightly enhanced the transport of BCs in high salt solutions. BSA and Cyt adsorption onto BC surface decreased the negative charge of BC and resulted in a less repulsive interaction in low salt solutions. In high salt solutions, the adsorbed BSA layers disaggregated BCs and reduced the strength of the interaction between BC and the sand. Adsorbed Cyt on BCs caused more attractive patches between BC and sand surface, and greater retention than BSA.

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1. Introduction

Biochar is a type of black carbon derived from low-temperature (<700 °C) pyrolysis of biomass (Lehmann et al., 2006; Lehmann, 2007a; Lehmann and Joseph, 2015). In recent years, biochar has been widely applied into soils to sequester carbon and mitigate atmospheric carbon dioxide, improve soil quality and structure, encourage microbial activity, increase crop production, and immobilize pollutants, such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), pesticides, and microbial pathogens (Lehmann, 2007b; Lehmann et al., 2011; Qian et al., 2016; Yavari et al., 2015). Conversely, relatively little is known about potential risks from mobile biochar particles in the field, such as colloid-facilitated contaminant transport (Zhang et al., 2010). Knowledge related to biochar particle mobility and fate in the subsurface under natural environmental conditions is therefore important for advancing the science behind field biochar application and evaluating the potential long-term risks (Wang et al., 2013a).

Several studies about the transport and retention of biochar particles in the subsurface have been investigated at the laboratory and field scales (Chen et al., 2017; Dittmar et al., 2012; Obia et al., 2017; Wang et al., 2013a; Yang et al., 2017a; Zhang et al., 2010). When the solution chemistry had the low ionic strength (IS) or high pH, fine biochar particles were easily transported with saturated water flow in porous media (Chen et al., 2017; Zhang et al., 2010). Biochar particles derived from lower pyrolysis temperatures and with smaller sizes exhibited greater mobility in porous media (Wang et al., 2013a). Furthermore, chemical heterogeneity played an insignificant role in the retention of nano-sized biochar particles.
2. Materials and methods

2.1. DOM

Suwannee River humic acid (SRHA, 2S101H, International Humic Substances Society) and Suwannee River fulvic acid (SRFA, 2S101F, International Humic Substances Society) were used as representative HS. In this study, Bull Serum Albumin (BSA, A7030, Sigma) and Cytochrome c from bovine heart (Cyt, C2037, Sigma) were used as the typical proteins commonly found in natural environments. BSA and Cyt are less water soluble globular proteins, which are ubiquitous in nature (Furkan et al., 2017; Huangfu et al., 2013; Sheng et al., 2016). These four DOM stock suspensions were all passed through a 0.45 μm filter (Jimlong Nylon Membrane Filters, Tianjin, CN). The concentration of each filtrate was determined from a mass balance after drying a sample suspension volume and then weighing the residue. All the stock solutions were stored in the dark at 4 °C until use.

2.2. Characteristics of biochar particles

The biochar used in this study was derived from pyrolyzing wheat straw (Zhengzhou, Henan Province, CN) at 600 °C for 1 h under limited oxygen conditions. The resultant biochar sample was allowed to cool at room temperature, and then a ball mill was used to grind it into powder form with a colloidal size range of 200–900 nm. This biochar powder (0.5 g) was added into 50 mL of deionized (DI) water to create a stock suspension and sonicated in a water bath for 10 min before use.

The elemental content of the biochar including carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) was determined with an Elemental analyzer (Flash 2000, Thermo Scientific, USA). The functional groups of biochar were analyzed using Fourier Transform Infrared spectroscopy (FTIR, Spectrum Spotlight 200 FT-IR microscopy, PE, USA). The sessile drop method was used to analyze the static contact angles of the biochar using a goniometer (JC2000D2, Powereach, CN). A Transmission Electron Microscope (TEM, JEOL JEM-1230, JPN) was used to study the morphology of BCs. A 50 mg L⁻¹ BCs suspension was prepared in the absence/presence of 5 mg L⁻¹ carbon concentration of DOM. The hydrodynamic diameter and electrophoretic mobility of bare BCs and DOM-coated BCs (DOM-BCs) were measured using a Zetasizer (Nano ZS90, Malvern, UK) under various solution chemistry conditions by adding 0.01 M HCl or NaOH solution and concentrated NaCl solution. All the experimental treatments are shown in detail in Table 1. For every sample measurement, at least three independent tests with no less than 15 cycles for each run were conducted. The colloidal stability of BCs was evaluated by examining the sedimentation profile of the particle suspensions under 10 mM NaCl (pH 7) and 1 mM NaCl (pH 5, 7, and 10) conditions, respectively. More details can be found in the supporting information (S1).

Experiments were performed to determine the adsorption of different DOM onto BCs (see section S2 in the supporting information). Electrophoretic mobilities (EPM) of BCs in the presence of DOM at three pH conditions were interpreted using Ohshima’s soft particle theory (Nakamura et al., 1992; Ohshima et al., 1992; Phenrat et al., 2010) which is summarized in Eqs. S1-S5 of the supplementary material. A nonlinear least square optimization algorithm (i.e., trust-region reflective Newton) with MATLAB (Natick, MA) was used to iteratively fit the EPM data using appropriate initial parameter values to obtain realistic estimates for three unknown parameters of Ohshima’s theory, i.e., charge density (Z/N0), layer thickness (d), and softness parameter (1/c) (Phenrat et al., 2010).

2.3. Porous medium

Quartz sand (grain size 0.425–0.600 mm, Sinopharm, China) was used as the porous medium in column experiments. To remove metal oxides, the sand was soaked in concentrated HCl solution for...
24 h, and then thoroughly washed with DI water. After that, the sand was dried at 105 °C for 8 h and baked at 600 °C for 4 h in a muffle furnace for removing organic matter (Tian et al., 2015). The cleaned sand was stored in PTFE plastic bottles until use. The ζ-potential of the sand under various solution chemistry conditions was determined using the following procedure: the sand was ground to powder and added to an electrolyte solution, the sand suspension was allowed to settle, and then the ζ-potential of the supernatant was measured using the Zetasizer.

### 2.4. Column experiments

Electrolyte solutions with selected NaCl concentrations and pH were prepared (Table 1). The pH and IS of the injection suspensions were adjusted by adding 0.01 M HCl or NaOH and NaCl solutions to the column for 3 PVs in the presence/absence of 5 mg C L⁻¹ suspension was injected into pore volumes (PVs) of background electrolyte solution were continued by injection of 5 PVs of biochar and DOM free background electrolyte solution to run in an upward mode using a peristaltic pump, and BC suspension was allowed to settle, and then the ζ-potential of the supernatant was measured using the Zetasizer. After recovery of the BC breakthrough curve (BTC), the column was carefully sectioned into 12 layers of approximately 1-cm segments to determine the spatial distribution of retained BCs. The excavated quartz sands were placed into a 50-mL glass flask with 20 mL of DI water, and shaken at 120 rpm for 4 h. The concentration of BCs in the suspensions was determined using the spectrophotometric method and the biochar recoveries of the whole column experiments were calculated as a function of depth. The initial injected BC amount, the masses of BC in the effluent, and retained BC in the sands were compared to obtain the mass balance.

Conservative tracer (3 mM NaNO₃) experiments were conducted in a similar manner to the BC BTC studies. In brief, 5 PVs of DI water were injected into the column, followed by 3 PVs of 3 mM NaNO₃ solution, and then 5 PVs of DI water. The concentration of NaNO₃ in the effluents was determined using UV-VIS spectrophotometer and calibration curve at a wavelength of 235 nm (Shang et al., 2010). The dispersivity was obtained by fitting NaNO₃ BTC using the one-dimensional convection-dispersion equation in the HYDRUS-1D software (Simunek et al., 1998). This software was also used to simulate BC transport and retention in porous media under the various solution chemistry conditions (see section 5 in the supporting information). Two kinetic retention sites were employed, one which considered first-order attachment and detachment, and the other irreversible, depth-dependent retention.

### 3. Results and discussion

#### 3.1. Characteristics of biochar and DOM

The TEM image of BCs in Fig. 1 shows that the morphology consists of an irregular shape and rough surface. The average hydrodynamic size of BCs was determined to be 457.2 ± 110.6 nm by the DLS method (Fig. S1). The chemical composition of the wheat straw-derived biochar was C (60.2%), H (1.6%), O (37.2%), N (0.5%), and S (0.5%), and the FTIR spectra of the biochar (Fig. S2) showed...
the presence of —COOH, C—H in-plane, —OH, C—O, and aromatic C==C and C—H functional groups (Yang et al., 2017b). Fig. 2 shows that the ζ-potential of bare BCs (absence of DOM) varied from −29.9 mV at pH 4 to −51.4 mV at pH 10 in 1 mM NaCl solution due to deprotonation of surface functional groups. An increase in IS from 1 to 10 mM NaCl at pH = 7 produced an increase in ζ-potential for bare BCs from −51.1 mV to −42.1 mV (Table 1) due to the influence of counter ions. The contact angles of BCs were 122.6 ± 3.0°, 99.7 ± 8.4°, and 0° in the presence of water, glycerinum, and n-decane, respectively (Yang et al., 2017b). The biochar material was therefore considered to be hydrophobic, and Lewis acid-base interactions were included in the interaction energy calculations discussed below.

### 3.2. Biochar colloid properties in presence of DOM

The HA, FA, BSA, and Cyt properties are shown in Table S1, and the ζ-potential plots of HA, FA, BSA, and Cyt in 1 mM NaCl solution as pH varying from 4 to 10 was presented in Fig. S3. The HA, FA, and BSA showed negative ζ-potentials with the absolute value trend (BSA < FA < HA) at a given pH, and Cyt was positively charged under most pH conditions. Other studies also showed that the ζ-potentials of HA were −20 mV at pH 3.5 and −44 mV at pH 10 (Mohd Omar et al., 2014), the ζ-potentials of FA were −35 mV at pH 2 and −60 mV at pH 10 (Palomino and Stoll, 2013), and the points of Cyt and BSA zero charge were around 10.4 and 4.7 (Salgin et al., 2012; Sheng et al., 2016).

The ζ-potentials and hydrodynamic diameters of BCs in the absence/presence of DOM under varying solution chemistry conditions are presented in Fig. 2, S4 and Table 1. Compared to the bare BC (from −29.9 mV at pH 4 to −51.4 mV at pH 10), the BCs showed more negative surface charge under FA coating (from −42.0 mV at pH 4 to −52.4 mV at pH 10) and HA coating (from −38.0 mV at pH 4 to −54.5 mV at pH 10). Other researchers have also reported that adsorption of HA and FA onto the surface of particles increased their negative charge (Dong et al., 2016; Wang et al., 2013b; Zhang et al., 2013). In contrast, the BCs showed less negative apparent surface charge when BSA (from −18.8 mV at pH 4 to −48.3 mV at pH 10) and Cyt (from −8.7 mV at pH 4 to −24.4 mV at pH 10) were adsorbed on its surface, because bare BC was more negatively charged than BSA and Cyt (Fig. S3). The negative charge density on the surface of multi-walled carbon nanotubes after coated BSA was similarly found to decrease over pH 4 to 11 (Bogzeiyik and Kopac, 2016). When the solution IS was increased from 1 mM to 10 mM, the negative ζ-potentials of BCs in the absence and presence of DOM decreased significantly and slightly, respectively (Table 1). One potential explanation is that adsorbed long-chain DOM reduced the compression of the double layer when the salt concentration became high. HA coating also resulted in a minor decrease in the ζ-potential of polyvinylpyrrolidone-coated Ag nanoparticle (PVP—AgNP) when the IS was increased from 0.5 to 5 mM (Wang et al., 2015). In another study, the presence of NOM weakened the decrease in the absolute value of the negative surface charge on C60 nanoparticles when the salt concentration increased from 100 to 500 mM (Shen et al., 2015). The ζ-potential of MnO2 colloids with BSA coating similarly showed less decrease than that of bare MnO2 colloids when the NaNO3 solution concentration increased from 10 to 500 mM (Huangfu et al., 2013).

The hydrodynamic diameter of BC with/without DOM tended to decrease with an increase in solution pH (Fig. S4) because a more negative surface charge induced larger electrostatic repulsion (Table 1). The hydrodynamic diameters of BCs in the presence of HA and FA were only slightly different (ranging from 632 to 783 nm) because the ζ-potentials were similar. In contrast, the hydrodynamic diameter of BCs with BSA significantly varied from 1313 nm at pH 4–676 nm at pH 10, and that with Cyt from 1554 nm at pH 4–831 nm at pH 10. These differences were related to the less negative ζ-potentials of BSA and Cyt under acidic and neutral conditions which induced less repulsive electrostatic interaction and more aggregation (McKeon and Love, 2008).

### 3.3. Effect of DOM on BC transport in low salt solution

Fig. 3a presents the BTCs of BCs in the absence/presence of DOM in 1 mM NaCl solution at pH = 7. All the BTCs of BCs gradually reached a plateau, which indicated that the maximum retention capacity of the sand surface was far from filling and may therefore not be the critical factor in these column experiments (He et al., 2015). In comparison to bare BC, the presence of HS slightly promoted BC transport, whereas the mobility of BCs was greatly reduced in the presence of BSA and especially Cyt proteins (Fig. 3a). These trends were generally consistent with the ζ-potentials of BCs in the presence and absence of DOM in Fig. 2, with more negative ζ-potentials producing greater transport. HS have been similarly reported to enhance biochar and ZnO nanoparticles transport in porous media (Jones and Su, 2014; Wang et al., 2013b).

Fig. 3b shows the RPs for BCs with/without DOM in 1 mM NaCl
solution. Consistent with the BTCs, about 35%–75% of the injected BCs were retained on the sand surface (Table 1). The RPs exhibited a hyper-exponential shape (Fig. 3b), which meant that the retention rate of BCs was very high near the column inlet and then decreased rapidly as the depth increased. Wang et al. (2013a) similarly observed a lot of nano- or micro-sized biochar retention and hyper-exponential RPs in saturated porous media under a low IS condition. The total mass balance of BCs was good, ranging from 86.8% to 97.4% (Table 1).

3.4. Effect of DOM for BCs transport in acidic/alkaline solutions

Fig. 4 shows the BTCs and RPs of BCs with/without DOM in acidic (pH = 5) and alkaline (pH = 10) solutions when the IS = 1 mM NaCl. An increase in the solution pH increased the magnitude of the ζ-potential for the BCs and sand and the corresponding repulsive electrostatic interaction (Fig. 2 and Table 1), which produced less BC retention for a given solution chemistry condition (Fig. 3 and Table 1). This behavior agrees well with previous studies on the transport of biochar particles or other types of colloids with increasing pH (Xia et al., 2015; Yang et al., 2017b; Zhang et al., 2010). Less DOM adsorption also occurred on the BCs with increasing pH (Table S2). Similar to Fig. 3 at pH = 7, the presence of HS enhanced and proteins diminished the BC transport in comparison to bare BCs. Specifically, the effluent mass balance of the BTCs (Table 1) followed the trend Cyt < BSA < bare BC < HA < FA at pH = 5, and Cyt < BSA < bare BC < FA < HA at pH = 10. These trends correspond to the measured magnitudes of the ζ-potentials for the BCs (Fig. 2 and Table 1), with less negative (repulsive) ζ-potentials producing greater retention. Note that the effect of FA on biochar mobility was slightly greater than that of HA under acidic conditions due to a more negative surface charge than HA (Table 1). Similar to Fig. 3, RPs for BCs with/without DOM at pH 5 and 10 were also hyper-exponential in shape.

3.5. Effect of DOM on BCs retention in higher salt solution

Fig. 5 shows that the BTCs and RPs of BCs in the absence/presence of DOM in 10 mM NaCl solution at pH = 7. Comparison of Figs. 3 and 5 reveals that an increase in the solution IS from 1 to 10 mM NaCl increased the BC retention (Table 1) due to a decrease in the magnitude of the ζ-potential for the BCs and sand (Table 1), compression of the double layer thickness, and a corresponding decrease in the electrostatic repulsion. Similar results have been observed for studies with biochar particles or other colloids with increasing IS (Cheng et al., 2016; Fang et al., 2013; Rabemananjara et al., 2014; Yang et al., 2017b; Zhang et al., 2010). In addition, greater amounts of DOM adsorption also occurred on BCs with increasing IS (Table S2). HS and proteins always enhanced the transport of BCs at IS = 10 mM NaCl with the effluent mass balance following the order: bare BC < Cyt < FA < HA < BSA. Note this effluent mass balance order was not consistent with the results at IS = 1 mM and pH = 7 (Fig. 3); i.e., Cyt < BSA < bare BC < FA < HA. Consequently, the adsorbed DOM on the BCs produced a different effect at IS = 1 than at 10 mM NaCl. The effect of BSA on BC transport was much stronger than that of HS, and the reason might be that BSA had larger molecular weight and more BSA was adsorbed on the BCs, which caused the larger thickness of BSA adsorption layer (Table S3). Besides, BSA also caused the small hydrodynamic size of the BCs (Table 1), meaning that BSA inhibited the aggregation process of the BCs in 10 mM NaCl solution. In contrast, Cyt almost did not or slightly facilitated BC transport under 10 mM condition, and one major reason might be that the positively charged Cyt increased the surface charge heterogeneity of the BC surface and induced the attractive patch-charge interaction among BCs, as well as between BC and quartz sand (Sheng et al., 2016; Wu et al., 2018). Various explanations for this difference will be investigated in detail in the next section. Similar to Figs. 3 and 4, RPs for BCs in 10 mM NaCl solution showed a hyper-exponential shape and the presence of HS and BSA except Cyt lessened the retention of the BCs in sands (Fig. 5b).

3.6. Interaction energies and retention mechanisms

Table S4 presents interaction energy parameters between BC and the sand for the various solution chemistry conditions when using Eqs. S10–S13. Results indicate the presence of an insignificant secondary minimum, and a large energy barrier that should inhibit BC retention under all solution chemistry conditions. This finding is obviously not consistent with the experimental observations in Figs. 3–5. Table S5 presents similar interaction energy parameter information when steric interactions were also included using Eqs. S10–S13. S17–S19. The predicted energy barrier is much larger when considering steric interactions than in Table S4. This indicates that inclusion of steric interaction provides an even less plausible explanation for the observed BC retention behavior in Figs. 3–5 than Table S4.
Bare BC surfaces exhibit large amounts of roughness in Fig. 1. Adsorbed DOM may also induce nanoscale roughness on the BC surface (Fig. S7). Furthermore, the $\zeta$-potential of the DOM was different from the bare BC (Fig. S3), and this implies that absorbed DOM is expected to induce charge heterogeneity on the surface of the BCs, especially for BSA and Cyt proteins. In addition, nanoscale roughness and chemical heterogeneity are known to be ubiquitous on sand surfaces (Suresh and Walz, 1996; Vaidyanathan and Chi, 1991). Interaction energy parameters have been reported to be very sensitive to nanoscale roughness and chemical heterogeneity parameters (Bendersky and Davis, 2011; Bradford et al., 2017; Bradford and Torkzaban, 2013; Suresh and Walz, 1996). In particular, small fractions of nanoscale roughness have been demonstrated to locally eliminate the energy barrier to produce primary minimum interactions (Bhattacharjee et al., 1998; Hoek and Agarwal, 2006; Huang et al., 2010). The energy barrier height and strength of the primary minimum interaction is a function of the roughness parameters, the solution IS, and the $\zeta$-potential of the surfaces (Kim et al., 2009; Rijnaarts et al., 1999). Shallow primary minima occur when small amounts of nanoscale roughness occur on both interacting surfaces (Bradford et al., 2017; Bradford and Torkzaban, 2013), and colloid interaction in such shallow minima are sometimes subject to diffusive or hydrodynamic removal (Bradford et al., 2017; Bradford and Torkzaban, 2015). Chemical heterogeneity may also lower the energy barrier height and create strong primary minimum interactions on smooth surfaces (Bendersky and Davis, 2011; Bradford and Torkzaban, 2013). Consequently, spatial variability in nanoscale roughness and chemical heterogeneity on the sand and the BC surface provide a viable alternative explanation for BC retention in Figs. 3–5.

The nearly complete recovery of BCs following excavation of the sand into deionized water (82.2–97.4%) indicates that the vast majority of the retained BCs were weakly associated with the sand.
surface, even when positively charged Cyt (Fig. S3) was adsorbed onto the BCs (Table S2). This can be explained by alteration of the interaction energy profile by nanoscale roughness on both the sand and the BCs (Bradford et al., 2017). In particular, small amounts of nanoscale roughness have been demonstrated to control the interaction energy profile even in the presence of significant fractions of positive charge heterogeneity (Torkzaban and Bradford, 2016). When colloids are weakly associated with the solid surface, colloid immobilization will be controlled by lever arms arising from deformation and pore space geometry (Torkzaban et al., 2008). The torque balance is always satisfied at a location where the roughness height on the sand is greater than the colloid radius (Rahman et al., 2014; Treumann et al., 2014). Colloid retention at such locations has been referred to as surface straining (Treumann et al., 2014). Strained colloids are released following soil excavation because of the destruction of the pore structure and non-stationary lever arms when the sand continuously mixed (Bradford et al., 2009; Treumann et al., 2014). Furthermore, hyper-exponential RPs (Figs. 3–5) have been associated with straining processes (Bradford et al., 2006, 2007; Sun et al., 2015) and BCs (Wang et al., 2013a, b).

3.7. Mathematical modeling

The BTCs and RPs for BCs in Figs. 3–5 were simulated well ($R^2 > 0.926$) using the transport model with two kinetic retention sites (Table 1 and Figs. 3–5). Most of the BC retention was associated with the irreversible, depth-dependent retention site (>43.2%). The value of $k_{tr}$ tended to increase with the hydrodynamic diameter of the BCs, and to be highest in the presence of Cyt due to its larger hydrodynamic diameter and less negative ζ-potential (Table 1). The value of $k_{rel}$ was relatively insensitive to the presence and/or absence of other DOM for a given solution chemistry condition. Differences in the retention of bare BCs and in the presence of HA, FA, and BSA for a given solution chemistry were therefore mainly attributed to the retention parameters on the reversible kinetic site. However, detailed interpretation of $k_{det}$ and $k_{rel}$ values was hampered by differences in the amount (0.001–56.6%) and reversibility ($k_{det}$ ranged from $7.27 \times 10^{-6}$ to $3.34 \times 10^{-2}$ min$^{-1}$) of retention on this site.

4. Implications

The fate and transport of biomass-derived BCs in a subsurface environment have significant environmental implications for the land application of biochars for carbon sequestration, mitigation of climate change, or soil quality improvement. HS and protein are pervasive and are major fractions of DOM in soil and aquatic environment. This study showed that various DOM ubiquitously present in the environment had a different impact on BC mobility in porous media that depends on the solution chemistry conditions (e.g. pH and IS). This study improved our understanding of the effect of four representative DOMs on BC fate in saturated porous media. If biochar is being applied into the topsoil layer of the agricultural field with a high organic matter, the organic matter might cause more BCs leaching into deeper soil layers following irrigation, rain, and snow melting which may ultimately reduce the long-term effect of biochar application for improving the soil quality. If biochar is added into the soils with animal manure (which usually contains a huge amount of proteins), the negatively/positively charged proteins or the protein mixtures can inhibit the transport of BCs at low ionic strength because of electrostatic repulsion, and the negatively charged proteins can largely improve the stability of the BCs and thus enhanced the mobility of BCs at high ionic strength due to surface alterations. Differential effects of HS and protein suggest that the composition of DOM is an important factor to be considered when assessing the transport, fate and long-term application of biochar in soil and aqueous phase because biochar surface coatings (especially caused by HS and negatively charged protein) can potentially facilitate the mobility of BCs in an environment. The interaction of DOM and biochar should, therefore, be considered before application of a biochar to a particular environment. More intriguingly, it is likely that biomacromolecules (e.g. protein and HS) adsorption onto other colloids and nanoparticles may similarly influence their stability and mobility, and facilitate the transport of associated contaminants under certain environmental conditions.

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Appendix A. Supplementary data

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References


Morales, V.L., Zhang, W., Gao, B., Lion, L.W., Bisogni Jr., J.J., McDonough, B.A.,
Jones, E.H., Su, C., 2014. Transport and retention of zinc oxide nanoparticles in
Guggenberger, G., Rodionov, A., Shibistova, O., Grabe, M., Kasansky, O.A., Fuchs, H.,
Jung, B., O’Carroll, D., Sleep, B., 2014. The influence of humic acid and clay content on
the transport of polymer-coated iron nanoparticles through sand. Sci. Total
Environment 496, 155–168.
Sun, W., Zhang, C., Shi, W., Wang, C., Jiao, X., 2016. Heteroadsorption of 17a-ethyl
Suresh, L., Walz, J.Y., 1996. Effect of surface roughness on the interaction energy
between a colloidal sphere and a flat plate. J. Colloid Interface Sci. 183 (1), 19–27.
Tian, R., Yang, G., Li, X., Huang, C., Gao, X., Li, H., 2015. Observation of the unusual
Vaidyanathash, C., Chi, T., 1997. Aggregation and deposition in granular media under un-
Xia, T., Fortner, J.D., Zhu, D., Qi, Z., Chen, W., 2015. Transport of sulfided-reduced graphitic carbon nano-onion in sand: concentration-dependent retention mecha-


