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Transport of carboxyl-functionalized carbon black nanoparticles in saturated porous media: Column experiments and model analyses

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ABSTRACT

The aim of this study was to investigate the transport behavior of carboxyl-functionalized carbon black nanoparticles (CBNPs) in porous media including quartz sand, iron oxide-coated sand (IOCS), and aluminum oxide-coated sand (AOCS). Two sets of column experiments were performed under saturated flow conditions for potassium chloride (KCl), a conservative tracer, and CBNPs. Breakthrough curves were analyzed to obtain mass recovery and one-dimensional transport model parameters. The first set of experiments was conducted to examine the effects of metal (Fe, Al) oxides and flow rate (0.25 and 0.5 mL min^{-1}) on the transport of CBNPs suspended in deionized water. The results showed that the mass recovery of CBNPs in quartz sand (flow rate = 0.5 mL min^{-1}) was 83.1%, whereas no breakthrough of CBNPs (mass recovery = 0%) was observed in IOCS and AOCS at the same flow rate, indicating that metal (Fe, Al) oxides can play a significant role in the attachment of CBNPs to porous media. In addition, the mass recovery of CBNPs in quartz sand decreased to 76.1% as the flow rate decreased to 0.25 mL min^{-1}. Interaction energy profiles for CBNP–porous media were calculated using DLVO theory for sphere–plate geometry, demonstrating that the interaction energy for CBNP–quartz sand was repulsive, whereas the interaction energies for CBNP–IOCS and CBNP–AOCS were attractive with no energy barriers. The second set of experiments was conducted in quartz sand to observe the effect of ionic strength (NaCl = 0.1 and 1.0 mM; $CaCl_2$ = 0.01 and 0.1 mM) and pH (pH = 4.5 and 5.4) on the transport of CBNPs suspended in electrolyte. The results showed that the mass recoveries of CBNPs in NaCl = 0.1 and 1.0 mM were 65.3 and 6.4%, respectively. The mass recoveries of CBNPs in $CaCl_2$ = 0.01 and 0.1 mM were 81.6 and 6.3%, respectively. These results demonstrated that CBNP attachment to quartz sand can be enhanced by increasing the electrolyte concentration. Interaction energy profiles demonstrated that the interaction energy profile for CBNP–quartz sand was compressed and that the energy barrier decreased as the electrolyte concentration increased. Furthermore, the mass recovery of CBNPs in the presence of divalent ions ($CaCl_2$ = 0.1 mM) was far lower than that in the presence of monovalent ions (NaCl = 0.1 mM), demonstrating a much stronger effect of Ca^{2+} than Na^+ on CBNP transport. Mass recovery of CBNPs at pH 4.5 was 55.6%, which was lower than that (83.1%) at pH 5.4, indicating that CBNP attachment to quartz sand can be enhanced by

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decreasing the pH. The sticking efficiencies (α) calculated from the mass recovery by colloid filtration theory were in the range from 2.1×10^{-2} to 4.5×10^{-1}, which were far greater than the values (2.56×10^{-6}–3.33×10^{-2}) of theoretical sticking efficiencies (α_{theory}) calculated from the DLVO energy by the Maxwell model.

1. Introduction

Carbon nanomaterials, such as carbon nanotubes, fullerene, and graphene, have received considerable attention due to their unique physical and chemical characteristics, leading to mass production and widespread application in industrial, commercial, and environmental fields (Mauter and Elimelech, 2008; Volder et al., 2013; Zhu et al., 2010). During their life cycle from production to disposal, however, carbon nanomaterials are inevitably released into water and soil environments, which have resulted in a concern about their health and environmental impacts (Klaine et al., 2008; Nowack, 2007; Petersen et al., 2011). Studies are therefore necessary to understand the fate and transport of carbon nanomaterials in the environment. Soil-groundwater system is an important pathway for the spread of inorganic and organic contaminants as well as biocolloids such as viruses and bacteria in the environment (McCarthy and Zachara, 1989). For this reason, the fate and transport of carbon nanomaterials in soil media and aquifer materials are of great interest in environmental disciplines. Researchers have investigated the transport behavior of carbon nanotubes, fullerene, and graphene in porous media. In particular, the effects of solution chemistry (pH, ionic strength/composition, dispersant), flow conditions (flow rate, water saturation), and soil media (metal (hydr)oxide, grain size) on the mobility of carbon nanomaterials in porous media have been examined (Chowdhury et al., 2012; Espinasse et al., 2007; Jaisi and Elimelech, 2009; Kasel et al., 2013; Lanphere et al., 2013; Li et al., 2008; Liu et al., 2013a; Mattison et al., 2011; Tian et al., 2011).

Black carbon is a carbonaceous particle, which can be produced naturally or by human activities including wild fire, biomass pyrolysis for biochar production, and fossil combustion by vehicles. It is an incomplete combustion byproduct with diverse properties (Long et al., 2013). Few studies have been performed to examine the transport of micron- and nano-sized biochar in porous media. Zhang et al. (2010) have examined the transport and retention of biochar particles in angular translucent sand. They performed the saturated and unsaturated column studies to observe the influences of pH, ionic strength, and biochar particle size. Wang et al. (2013a,b) have investigated the transport of biochar particles in quartz sand under saturated flow conditions. They conducted column experiments to examine the effects of pyrolysis temperature, particle size, humic acid, and iron oxyhydroxide on the transport behavior of biochar in porous media. Meanwhile, carbon black is a nano-sized amorphous carbon powder, which can be produced industrially from hydrocarbons in petroleum and coal. It is a manufactured product with well-controlled properties, typically containing 90–99% elemental carbon (Asokan et al., 2013; Long et al., 2013; Sis and Birinci, 2009). Carbon black is widely used in chemical and industrial products or applications such as ink pigments, coating plastics, the rubber industry, and composite reinforcements (Ridaoui et al., 2006; Xu et al., 2007). Even though carbon black is strongly hydrophobic and tends to aggregate in water, it can be dispersed in aqueous media through surface functionalization or surfactant use (Kato et al., 2011; Ridaoui et al., 2006). Several studies have suggested that carbon black is potentially toxic to aquatic organisms (Baun et al., 2008; Cheng et al., 2007; Kennedy et al., 2008; Zhu et al., 2009). Carbon black may therefore adversely impact aquatic organisms and human health when released into the environment.

The aim of this study was therefore to investigate the transport behavior of carboxyl-functionalized CBNPs in porous media. Column experiments were performed for potassium chloride (KCl), a conservative tracer, and CBNPs under saturated flow conditions. Breakthrough curves (BTCs) of CBNPs and chloride were obtained by monitoring effluent, and then mass recovery, attachment rate coefficient, and sticking efficiency were quantified from these curves. Additionally, interaction energy profiles for CBNP-porous media were calculated using DLVO theory for sphere–plate geometry. The theoretical sticking efficiencies were also calculated by the Maxwell model from the DLVO energies.

2. Materials and methods

2.1. Carbon black nanoparticles

Carboxyl-functionalized CBNPs were purchased from Columbian Chemicals (Seoul, Korea) and used as-received. Transmission electron microscopy (TEM, JEM-1010, JEOL, Tokyo, Japan) was used to obtain images of CBNPs (Fig. 1a); the mean diameter of CBNPs was 21 nm. Fourier-transformed infrared (FTIR) spectrometry (Nicolet 6700, Thermo Scientific, Waltham, MA, USA) was used to obtain infrared spectra of CBNPs (Fig. 1b). This spectrum demonstrated the presence of carboxyl functional groups on the surfaces of CBNPs. Nitrogen gas (N_2) adsorption–desorption isotherm analysis using a surface area analyzer (BELSORP-max, BEL Japan Inc., Osaka, Japan) indicated that CBNPs have a BET specific surface area of 101.6 m^2/g and total pore volume of 0.463 cm^3/g.

Suspensions of CBNPs were prepared by mixing 5 mg CBNPs with 500 mL electrolyte solutions of 0, 0.1, 1.0, 5.0, and 10 mM NaCl. Suspensions were sonicated using an ultrasonicator (Q500, Qsonica, Newtown, CT, USA) with three cycles of sonication (5 min) at 5-min intervals to ensure thorough dispersion. The pHs of the suspensions were 5.4–5.8. Suspensions of CBNPs in electrolyte solutions of 0.01 and 0.1 mM $CaCl_2$ (pH of the suspension = 5.6–5.7) were also prepared following the same procedures as describe above. Scans of absorbance as a function of wavelength were performed for each of the sonicated suspensions using a UV–vis spectrophotometer (Genesys 10S, Thermo Scientific), and the optimal wavelength for CBNP concentration measurements was found to be 265 nm (Fig. 2). Calibration curves were prepared to establish the relationship between absorbance and concentrations of CBNPs ($R^2 > 0.99$). Zeta potentials of CBNPs were measured using an