Co-transport of Gold Nanospheres with Single-walled Carbon Nanotubes in Saturated Porous Media

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Abstract

Porous media transport of engineered nanomaterials (ENMs) is typically assessed in a controlled single-particulate environment. Presence of a secondary particle (either natural or engineered) in the natural environment though likely, is rarely taken into consideration in assessing ENMs' transport behavior. This study systematically assesses the effect of a secondary ENM (i.e., pluronic acid modified single-walled carbon nanotubes, PA-SWNTs) on a primary particle (i.e., gold nanospheres, AuNSs) transport through saturated porous media under a wide range of aquatic conditions (1-100 mM NaCl). AuNS hetero-dispersions (i.e., with PA-SWNTs) are transported through saturated sand columns, and the transport behavior is compared to AuNS-only homo-dispersion cases, which display classical ionic strength-dependent behavior. AuNS hetero-dispersion, however, is highly mobile with little to no ionic strength-dependent effects. This study also assesses the role of pre-coating of the collectors with PA-SWNTs on AuNSs' mobility, thereby elucidating the role played by the order of introduction of the secondary particles. Pre-existence of the secondary particles in the porous media shows enhanced filtration of primary AuNSs. However, the presence of natural organic matter (NOM) slightly increases AuNS mobility through PA-SWNT coated sand at 10 mM ionic strength. The study results demonstrate that the presence and order of addition of the secondary particles strongly influence primary particles' mobility. Thus ENMs can demonstrate facilitated transport or enhanced removal, depending on the presence of the secondary particulate matter and background solution chemistry.

Keywords: Co-transport; porous media; gold nanoparticles; single-walled carbon nanotubes; pluronic

1. Introduction

Increased use of engineered nanomaterials (ENMs) makes their environmental release highly likely whether the release is intentional as remedial agents, accidental from manufacturing processes, or inevitable at the end of life of ENM-containing products (Köhler et al. 2008, Nowack et al. 2012), highly likely. Regardless of routes of release and exposure (Khin et al. 2012, Köhler et al. 2008) sediments and porous subsurface have been identified as likely environmental sinks for ENMs (Gottschalk and Nowack 2011), in which the ENMs undergo subsequent transport and transformation (Lowry et al. 2012). Fate and transport, the primary process controlling ENM exposure and risk, is at the center of the nano-environmental health and safety (nano-EHS) research (Petosa et al. 2010), which devotes most of its efforts to determining appropriate fate descriptors (deposition rate and efficiency or transport distances) with single-particle breakthrough studies (Petosa et al. 2010, Xin et al. 2016) or by studying deposition onto polished crystal surfaces (Chang and Bouchard 2013, Quevedo and Tufenkji 2009). Although a reliable prediction of ENM transport is the ultimate goal of nano-EHS studies, most, if not all, are performed in clean and controlled environmental platforms.

State-of-the-art ENM transport studies have systematically evaluated the effects of various material properties and background chemistries of a wide set of materials (Petosa et al. 2012), e.g., fullerenes (nC₆₀), carbon nanotubes (CNTs), nano-scale zero-valent iron (nZVI), titanium dioxide (TiO₂), zinc oxide (ZnO), and silver nanoparticles (AgNPs). The influence of solution chemistry [pH and Ionic Strength (Godinez and Darnault 2011), organic matter (Thio et al. 2011)], ENM characteristics [size and size distribution (Phenrat et al. 2009), concentration (Phenrat et al. 2009), shape (Afrooz et al. 2013b), surface charge (El Badawy et al.

2013), synthesis method(Chowdhury et al. 2012a), surface coating(Tripathi et al. 2011), and magnetic properties(Hong et al. 2009)], collector properties [grain size distribution(Mattison et al. 2011) and flow conditions (Cai et al. 2015)] on ENMs' mobility have also been reported. In addition to the aforementioned experimental investigations, efforts have been made to predict and validate ENM transport theoretically by employing clean-bed filtration theory (CFT)(He et al. 2009). However, experimental and theoretical studies of ENMs in homogeneous and single particulate systems have limited transferability to the natural environment in the presence of natural particles and other ENMs(Hotze et al. 2010).

Appreciating the need for assessment of environmental complexities, numerous studies have been conducted to delineate the effects of physical [i.e., surface roughness(Song and Elimelech 1994) and shape(Saiers and Ryan 2005)] and geochemical [i.e., surface charge(Song et al. 1994), surface coating(Joo et al. 2009), and mineralogical compositions(Kim et al. 2012)] heterogeneities of the collectors on ENM transport. Furthermore, the effect of pre-coating(Joo et al. 2009, Tong et al. 2010) the collector surfaces with natural organic matter (NOM), clay, or biofilm has also been evaluated, where ENM mobility is reported to decrease due to the competition between the ENMs and the NOMs for available attachment sites or to increase due to the availability of increased surface sites of the secondary particle coated collectors for NM deposition(Chowdhury et al. 2012a, Tong et al. 2010). The altered nanomaterials transport behavior in the presence of secondary entities necessitates further studies to assess the effects of environmental complexities on porous media transport of ENMs.

Altered interfacial interaction of the ENMs may also result from the co-existence of multiple particulate entities in the column influent suspension (Afrooz et al. 2013a, Cerbelaud et al. 2008, Huynh et al. 2012). These studies were performed with aquatic suspensions to

understand their aggregation behavior under certain ionic strength conditions, but do not provide any information regarding the sub-surface transport processes of ENMs. ENM co-transport studies are needed to better understand of the influences of secondary entities; i.e., ENMs, bio-particles, or natural nanoparticles (co-dispersed with the primary ENM or pre-deposited on collector surfaces), on the transport of the primary particles through porous media. Thus far, ENM co-transport literature primarily assessed the effects of bacterial presence on ENM transport behavior; e.g., TiO_2 transport was observed to have enhanced in a co-transport scenario compared to that of TiO_2 -only case (Chowdhury et al. 2012a, Wang et al. 2012). Reduced bacterial mobility in the presence of CNT has also been reported (Yang et al. 2013a) at an elevated ionic strength (25-100 mM). Additionally, the effect of natural nanomaterials (NNM) on ENM transport has been reported (Wang et al. 2015): goethite nanoparticle showed an enhanced mobility of nano-hydroxyapatite at circumneutral pH due to heteroaggregation between the two particles. Such evidences suggest that ENM transport through porous media is strongly influenced by the presence of a secondary particulate entity, the likely mechanism being higher collision and facilitated filtration.

However, transport studies with multiple ENMs are scarce in ENM fate and transport literature. To-date, only two such studies have been reported: TiO_2 transport with multiwalled carbon nanotubes (Wang et al. 2014) and co-transport of TiO_2 and nC_{60} (Cai et al. 2013). These studies reported significant differences in the mobility of the primary TiO_2 in singular and binary matrices (in the presence of secondary nC_{60} s or CNTs) with strong pH and ionic strength dependence. Similarly, when TiO_2 was used as a secondary particle, transport of CNTs decreased under all examined conditions. However, both of these studies used matrices in which primary and secondary particles would undergo simultaneous deposition at higher ionic strength (i.e.,

representing brackish or saline condition); thus they preclude enumeration of underlying transport mechanisms over a wide range of ionic strength. Therefore, contribution of the reported studies is restricted to low ionic strength (0.1-10 mM) conditions with limited environmental relevance. To summarize, mechanistic co-transport studies appear to be a persistent data gap in the ENM fate and transport literature, and the role of a wide range of environmentally relevant ionic strength conditions, presence of NOM, and the order of addition of the secondary particles need to be systematically assessed.

The objective of this study is to investigate transport of a model nanoparticle, i.e., gold nanospheres (AuNSs), in the presence of a well-characterized secondary ENM, i.e., single-walled carbon nanotubes (SWNTs). This study contributes to addressing the existing data gaps by providing a mechanistic understanding of ENM co-transport behavior over a wide range (1-100 mM) of ionic strength for a new ENM duo (AuNS-SWNT). In order to mechanistically assess the filtration mechanisms, especially at elevated ionic strengths, inherent SWNT-SWNT interaction is eliminated via nonionic pluronic acid (PA) functionalization (Afrooz et al. 2013a). A range of PA concentrations is utilized to generate PA-SWNTs with desirable stability, i.e., highly stable suspensions are used for co-transport studies, whereas, SWNTs with lower stability are used to pre-coat the collector surfaces. Co-transport under a wide range of ionic strength (1-100 mM NaCl) is studied and compared with primary AuNS transport. The effect of NOM on AuNS transport is also monitored for typical groundwater conditions (i.e., 10 mM total ionic strength). This is a first-of-its-kind study to mechanistically assess co-transport of AuNSs (in the presence of another ENM) over a wide range of ionic strengths. The results from this study can be considered the initial step to attain a more reliable assessment of ENM co-transport through porous media in cases of multiple ENMs' presence in an aquatic environment.

2. Materials and Methods

2.1 Preparation of AuNS Suspensions

Poly (acrylic acid) or PAA-coated AuNS suspension at a concentration of 50 mg/L was procured from Nanopartz Inc. (Loveland, CO). The supplier reported 10 nm nominal diameter for the AuNSs. Procured AuNSs were diluted 4 times to achieve a concentration of 12.5 mg/L for all transport experiments.

2.2 Preparation of PA-SWNTs

Dry SWNTs, produced by high-pressure carbon monoxide disproportionation or HipCO method (Bronikowski et al. 2001) was obtained from Tubes at Rice (Houston, TX). The supplier reported that average diameter and length of the SWNTs were 1.03 nm (a range of 0.7-1.45 nm) and 0.93 μm (a range of 0.1-2.6 μm), respectively. Commercially available pluronic acid (PA) F-127 was obtained from Sigma Aldrich (St. Louise, MO); and 0.02, 0.1, 1, and 5% (w/v) PA solution was prepared using filtered (0.45 μm inorganic membrane filters, VWR international LLC, Radnor, PA) deionized (DI) water (Millipore, Darmstadt, Germany). The PA solutions were prepared by magnetic stirring for 1 h at room temperature.

10 mg of procured SWNTs was added to 100 mL (0.02, 0.1, 1, and 5%) of PA solution and sonicated in an ice bath for 1 h employing an S-4000 ultrasonicator (Misonix, Inc. Farmingdale, NY) at a controlled input energy of 100–105 kJ. The sonicated samples were quiescently left aside for 24 h and the supernatant was decanted and centrifuged at 12000 $\times g$ for 1 h with a Beckman Coulter (Brea, CA) centrifuge. The supernatant of the centrifuged samples was then decanted and used for subsequent experiments.

2.3 Solution Chemistry

All transport experiments were performed in the presence of monovalent NaCl at 1, 10, 30, and 100 mM concentrations. A 5M NaCl stock solution (BDH Chemicals) was purchased from VWR (Radnor, PA) and diluted with filtered DI water to obtain the solution at appropriate ionic strength. The pH of the salt solutions was left unadjusted (ambient) and determined to be 6.56 ± 0.04 . Suwannee River humic acid or SRHA (Standard II, 2S101H, International Humic Substances Society, St. Paul, MN) at 2.5 mg TOC/L was used as the representative NOM. SRHA solution was prepared by dissolving 5 mg of dry powder in 100 mL DI water and by magnetically stirring for 30 min. The solution was then filtered through 0.45 μm syringe filters (PES filters, Thermo Scientific, Pittsburgh, PA). TOC equivalence was used and measured with a TOC analyzer (TOC-VCSH, Shimadzu Corp., Japan). The SRHA stock solution was stored in the dark at 4 °C.

2.4 Physicochemical Characterization

Physical morphology of the AuNSs and SWNTs was characterized using a JEOL 2010F Transmission Electron Microscope (TEM) at the Texas Materials Institute. Copper-carbon TEM grids were prepared with ENM suspensions at desired particle concentrations and dried at 60 °C for 15 min. Bright field imaging and high-resolution (HR) microscopy techniques were utilized to investigate the particle size and shape.

DLS was employed to characterize the size of the ENMs in the experimental matrices. Details of the DLS technique have been described elsewhere (Saleh et al. 2008). Briefly, 2 mL ENM suspension was added into a clean borosilicate glass vial under appropriate solution

chemistry. A 632.8 nm laser (ALV CGS-3 goniometer system, Langen, Germany) shone through the vial and scattered light was detected at 90° and converted to hydrodynamic radii (HR) employing an auto-correlator and cumulant analysis. HR data were collected every 10 s for a 30 min duration.

To assess and confirm the chemical identity of the AuNS, an Agilent 8454 UV-vis spectrophotometer (Santa Clara, CA) was used. AuNS suspensions were prepared and injected to a flow through cell of 300 µL volume. Spectral response was collected for the entire UV and visible range (200-1100 nm).

2.5 Electrokinetic Characterization

Electrophoretic mobility (EPM) of the ENMs in their homogeneous and heterogeneous dispersion states were evaluated using a Malvern Zetasizer (Malvern Instruments Ltd., Worcestershire, UK) at pH 6.7±0.1 and at a temperature of 20 °C. For each condition, 800 µL sample was injected into the disposable capillary cell (DTS 1070) ensuring that the sample was brought in contact with the electrodes without any introduction of air bubbles. Four different cells were used for AuNS, PA-SWNT (0.02%), PA-SWNT (5%), and AuNS-PA-SWNT (5%) suspensions. Cells were flushed 10 times with DI water between each measurement. A total of 3 replicates were taken for every measurement to ensure reproducibility. NaCl concentrations of 1, 10, 30 and 100 mM were considered for all the suspensions. Experiments investigating the effects of NOM were performed at 10 mM ionic strength conditions.

2.6 Column Experiments

2.5 cm diameter and 10 cm long, Kontes Glass columns (Kimble Chase, Vineland, NJ) were packed with Ottawa sand (Fischer Scientific, Waltham, MA). The 20-30 mesh sand was carefully washed and cleaned following a detailed cleaning protocol described elsewhere (Saleh

et al. 2007). In brief, the Ottawa sand was saturated in DI water overnight and then boiled for 10 min followed by bath sonication and subsequent washing to remove impurities and colloids. The sonication procedure involved multiple sonication-rinsing cycles (10 min sonication and 2 min rinsing). Each sonicated batch was rinsed three times and the supernatant was decanted prior to the next cycle of sonication. In total, 15 such sonication-rinsing cycles were used to remove all loosely bound colloids and impurities. The cleaned sand was then soaked overnight in concentrated hydrochloric acid (HCl) to remove any metallic impurities. The sand collectors were then washed with DI until the pH reached 6.5; this was followed by an additional cycle of soaking with 50 mM CaCl_2 . An additional 5 cycles of sonication-rinsing were performed to remove tightly bound colloids from the collector surfaces. Such extensive cleaning of the sand was necessary to de-convolute the breakthrough signal from any potential release of pre-existing colloids that are typically present in the as-received sand. The cleaned sand was then dried at 80 °C and stored in an airtight container. The cleaned sand was re-sieved with 20-25 mesh sieve, to attain a narrower grain size of 707-841 μm .

The Kontes columns were dry-packed (Jaisi et al. 2008) following a layer-by-layer packing process, where 1-cm layers were poured in and compacted with a wooden bar. A vibrator was used to ensure uniform packing and eliminate stratification. Carbon dioxide gas was made to flow through the column for 20 minutes to remove all air from the pore spaces. The column was saturated by pumping DI water (Figure S1) for 8 h via an Ismatec precision variable-speed peristaltic pump purchased from IDEX Inc. (Wertheim, Germany). Porosity of the packed beds was determined gravimetrically by weighing the column before and after DI saturation, and was found to be 0.376 ± 0.013 . After the saturation of the column, tracer studies were performed using 4 pore volumes (PVs) of lithium bromide (LiBr) solution. The tracer was monitored

continuously at 197nm wavelength using aUV-vis detector(Agilent Technologies, Santa Clara, CA). Prior to the introduction of the ENMs, the packed column was flushed with at least 4 PVs of appropriate background solution. The approach velocity of the tracer and the carrier solution was adjusted to 0.003 cm s^{-1} (equivalent to a volumetric flow rate of 1 mL min^{-1}). ENMs were then introduced at the same background electrolyte concentration as a finite pulse (4PVs). The pulse was followed by the injection of the respective electrolyte solution for 4 more PVs. Subsequent injection of DI water was performed to monitor ENM release. For each new experiment, a cleaned and newly packed column was used.

The effluent concentration was measured using pre-established calibration curves (Figure S2) for AuNS, PA-SWNTs, and AuNS-PA-SWNT hetero-dispersions. Dilution factors of 2, 4, 6, and 8 to the stock AuNS suspensions were used to obtain a calibration curve at 517 nm using a flow through cell (Agilent Technologies, Santa Clara, CA) of 300 μL volume. For PA-SWNTs, 5, 10, 20, 40 dilution factors were used to develop a calibration curve at 235 nm. Calibration curves obtained for the AuNS and PA-SWNTs resulted in an R^2 value of 0.9999 for both cases (Figure S2).A calibration curve was also obtained for AuNS-PA-SWNTs hetero-dispersion, at their characteristic wavelength of 517 nm, which resulted in an R^2 value of 0.9998 (Figure S2). For the ENM transport studies, AuNS and PA-SWNTs (0.02%, 0.1%, 1%, and 5%) were flowed through the saturated column under varying ionic strength (1-100 mM NaCl). The concentration of the column effluent was continuously monitored every 15 s (approx. 0.02 PV) for the entire duration of the experiment. At least one replicate run (through a freshly packed column) was performed under each ionic strength condition.

Co-transport experiments were performed flowing a hetero-dispersion of AuNS-SWNT (at a mass ratio of 1:5 for SWNT:AuNS). Also, a sequential flow of PA-SWNT and AuNS was

made, where 4 PV of PA-SWNTs was made to flow through the sand-packed column under a certain ionic strength (to pre-coat the collector surfaces) followed by 4 PV of AuNS injection at the same ionic strength. Co-transport and sequential-transport experiments were carried out at electrolyte concentrations identical to the “AuNS-only” cases.

3. Results and Discussions

3.1 Morphological and Chemical Properties

Figure S3 presents representative high-resolution transmission electron micrographs of AuNS and SWNTs. AuNSs have spherical morphology with an average diameter of 12.9 ± 1.7 nm (Figure S3a). SWNTs are found to be well-dispersed within the dispersion media (Figure S3b). A significant number of dark spots are observed in the PA-SWNT images, which are probably metal catalysts used for SWNT synthesis. Elemental analysis (EDS) of the samples confirms the presence of iron (Fe) catalysts in the sample.

The chemical signature of the AuNS and surface properties of the PA-SWNTs were further evaluated using UV-vis and Raman spectroscopy, respectively. The AuNSs (16.67 mg/L) show a characteristic peak at 517 nm (Figure S4a) with an absorbance of 0.347 a.u. (Soejima et al. 2011). Raman spectroscopy of the SWNTs confirms the presence of characteristic defect or D and graphitic or G peaks at 1330 and 1595 cm^{-1} , respectively (Figure S4b). The attenuation of the D/G ratio of SWNTs from 0.5580 to 0.1778 for pristine and PA-SWNTs (dispersed in 5% PA), respectively, indicates effective surface coverage of PA. Similar attenuation of D/G has previously been reported in the literature for such non-covalent functionalization (Georgakilas et al. 2002).

The DLS-measured average hydrodynamic radii (HR) of AuNSs and PA SWNTs in DI water are 18.9 ± 1.2 and 180.5 ± 15.8 nm, respectively (Figure S5). However, the hetero-dispersion

of AuNS-SWNT shows an average HR of 41.4 ± 10.4 nm. The reduction of particle size in the hetero-dispersion is likely the result of the averaging of smaller AuNSs with a lower concentration of relatively larger sized PA-SWNTs, as the CONTIN algorithm provides overall intensity-averaged particle sizes over the measurement period.

3.2 Electrokinetic Properties

ENMs demonstrate a decreasing trend in the absolute values of the EPMs with increase in electrolyte concentration (Figure S6), supporting the classical electrokinetic behavior of charged particles (Jaisi et al. 2008, Saleh et al. 2007). EPMs of AuNSs decrease from $-(2.78 \pm 0.18)$ to $-(1.63 \pm 0.23) \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ S}^{-1}$ for an increase in NaCl concentration 1 to 100 mM. The origin of the negative surface potential is likely from the PAA polyelectrolyte (negative carboxyl moieties) coatings and is consistent with previously reported literature values (Afrooz et al. 2013a, Afrooz et al. 2013b, Fresnais et al. 2013). However, EPMs for both 0.02% and 5% PA-SWNTs do not vary substantially, i.e., $-(0.35 \pm 0.03)$ and $-(0.29 \pm 0.03) \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ S}^{-1}$ to $-(0.03 \pm 0.03)$ and $-(0.03 \pm 0.02) \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ S}^{-1}$, respectively for the same increase in NaCl concentration. Since PA is a nonionic polymer, these low values of EPMs confirm that effective coating of the SWNT surfaces occurs with these polymers, and that the likely stabilization has occurred from steric interaction between the sorbed polymer layers (Moore et al. 2003, Vaisman et al. 2006). For the hetero-dispersion of AuNSs and 5% PA-SWNTs, changes in NaCl concentration from 1 to 100 mM result in an EPM decrease from $-(1.02 \pm 0.23)$ to $-(0.18 \pm 0.02) \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ S}^{-1}$. These values are intermediate to the EPM values of AuNS and PA-SWNT homo-dispersions. Since electrophoresis is an optical technique that monitors average scattering from particle diffusion under an electric field, the overall reduction in EPM values for

the hetero-dispersion may be due to the averaging of low EPM nonionic PA-coated SWNTs with the higher EPM AuNSs.

3.3 Transport of AuNS Homo-dispersions

Transport behavior of the AuNS homo-dispersions is presented in Figure 1 as a function of NaCl concentrations. Background electrolytes significantly influence the AuNS transport through the sand column, as their mobility decreases with an increase in electrolyte concentration. The % eluted is estimated (by numerical integration) as $96.9 \pm 4.6\%$ of the influent mass for 1 mM NaCl case. Such negligible deposition at lower ionic strength indicates strong electrostatic repulsion between AuNSs and collector surfaces. Other mechanisms of filtration, i.e., straining are not significant, because the size ratio of the AuNS and the sand grains (i.e., 0.0003) is much lower than the literature-reported favorable colloids/media diameter ratio (i.e., 0.005) for physical filtration (Bradford et al. 2004). AuNS mobility is the lowest in the presence of 100 mM NaCl with a breakthrough plateau of 0.49 ± 0.03 and elution of $40.0 \pm 2.3\%$. The decreasing trend of the elution of the AuNS homo-dispersion through the sand column with increasing ionic strength can be explained by the corresponding reduction in electrostatic double layer interaction as is evident in Figure S6. These results corroborate similar findings (Jaisi et al. 2008, Saleh et al. 2007) for other negatively charged ENMs, e.g., CNT and nZVI particles.

Each breakthrough profile was followed by a release curve obtained by flowing DI water through the column (Figure S7). At low ionic strength, (i.e., 1 mM NaCl) no detachment or release of the deposited AuNSs was observed (hence not shown in Figure S7). A numerical integration (using discretized trapezoids) of the release curves suggest that 57%, 87%, and 86%

of the retained material has been released when the solution chemistry changed to DI from 10, 30, and 100 mM NaCl, respectively. The shape of the breakthrough and the increasing release percentages with increased salt concentrations suggest that the AuNS deposition onto the sand surface is primarily electrostatic and is at the secondary minima. The observed detachments of the particles can be attributed to removal of particles from the secondary energy well as observed earlier for other ENMs, e.g., SWNTs and nano cerium dioxide (Jaisi et al. 2008, Li et al. 2011).

3.4 Transport of PA-SWNT Homo-dispersions

SWNTs, dispersed in a wide range of PA concentrations (0.02-5%), were injected through sand columns at low (1 mM) and high (100 mM) electrolyte conditions. At low ionic strength, the effect of PA functionalization on SWNT mobility is negligible (Figure S8). Even though the EPMs of the PA-SWNTs slightly decrease (Figure S6) with an increase in the amount of PA used in dispersion, the breakthrough plateau and retention percentages of the SWNTs are similar for the entire range of PA. The average retention of the PA-SWNTs at 1 mM NaCl, for the entire range (i.e., 0.02-5%) of PA, is $6.9 \pm 1.5\%$ (Figure S8). Filtration of PA-SWNTs at low ionic strength with no detectable releases can be attributed to the physical removal mechanism for the PA-SWNTs, which is inconsistent with the previous findings (Chowdhury et al. 2012b, Jaisi et al. 2008).

At 100 mM NaCl, however, the amount of PA used in dispersing SWNTs demonstrates significant influence on their transport behavior (Figure 2). The percent breakthrough of PA-SWNTs increases with the increase in PA concentrations. The elution of 5% PA-SWNTs is found to be $92.9 \pm 3.3\%$ compared to $29.1 \pm 6.4\%$ for the 0.02% PA case. Percent eluted is estimated as 57.4 ± 8.6 and 71 ± 4.5 for 0.1 and 1% PA, respectively. The increased mobility of PA-SWNTs with the increase in PA concentration has likely resulted from a steric interaction

between attached nonionic PA macromolecules on the SWNT surfaces (Saleh et al. 2010). Enhanced transport via similar surface modification of SWNTs has been reported earlier (Bouchard et al. 2012, Tian et al. 2012). The shape of the PA-SWNT breakthrough curves at 100 mM NaCl is to be noted as it does not follow the tracer or other PA-SWNT transport trends, but rather shows a gradual increase over time with no plateau at the end of the pulse injection. Such behavior can be attributed to progressive blocking of available deposition sites as described in earlier studies (Bradford and Bettahar 2006, Kasel et al. 2013). Continual injection of PA-SWNTs blocks the available surface sites on the sand collectors via attachment of the SWNTs over time. Thus subsequent PA-SWNT injection results in SWNT-SWNT interaction between SWNTs in pore water and SWNTs that have already coated the collector grains. Longer PV flushing causes complete recovery of these PA-SWNTs after 15 PV (Figure S9), when all available deposition sites onto the collectors have been exhausted and been coated with the SWNTs.

3.5 Transport of AuNS & PA-SWNT Hetero-dispersions

The role of PA-SWNTs on AuNS transport is evaluated by performing transport experiments of AuNS-PA-SWNT hetero-dispersions. This scenario simulates coexistence of primary AuNS and secondary SWNTs in the pore water. SWNTs dispersed in 5% PA solution were used to prepare the hetero-dispersions (ensuring minimal surface interaction with PA-SWNTs). Figure 3 presents the breakthrough profiles (Figure 3a) and corresponding elution percentages (Figure 3b) determined from the co-transport experiments. The maximum C/C_0 values (i.e., from 0.99±0.007 to 0.96±0.01) and %eluted (i.e., 98.0±1.2% to 79.1±3.2%) decrease with the increase in NaCl concentration from 1 mM to 100 mM. Though the strength of the electrolytes showed minimal effect on the breakthrough plateau of the co-transport of AuNSs, the shape of the

breakthrough profiles shows unique differences between high and low electrolyte conditions. AuNS hetero-dispersion breakthrough shapes (Figure 3a) deviate from those of the homo-dispersion case (Figure 1a), but closely resembles the shapes of 5% PA-SWNT breakthrough (Figure 2a). The observed resemblances suggest that higher mobility of the AuNSs is likely due to their facilitated co-transport with highly mobile 5% PA-SWNTs, even at high electrolyte strength. The filtration of AuNSs likely has occurred via facilitated removal of PA-SWNTs, where AuNSs nucleated around the PA-SWNTs at elevated ionic strength conditions. Similar observations have been reported elsewhere for AuNS hetero-aggregation (Afrooz et al. 2013a). Transport mechanisms describing similar enhanced mobility of titanium dioxide (TiO_2) in the presence of CNTs have also been reported earlier (Wang et al. 2014). Such preferential attachment of the negatively charged AuNSs onto the PA-SWNTs, instead of onto the collector surfaces, can be explained by unfavorable electrostatic interaction between these surfaces (Figure S6)—i.e., charged AuNSs and likely charged sand surfaces with -40 mV (Johnson et al. 1996) to -25 mV (Saiers and Lenhart 2003) surface potential at 10 mM to 100 mM NaCl concentration—compared to electrostatically favorable AuNS and PA-SWNT interaction (with PA-SWNT EPM values of -3.5 mV to -0.6 mV at 1 mM to 100 mM NaCl concentration). Furthermore, an order of magnitude smaller size of the SWNTs (compared to sand grains) provides additional (by an approx. factor of 1.5) surface area for the AuNSs to attach (Table S1 to S3).

Release curves of the co-deposited AuNSs in the presence of 30 and 100 mM NaCl (no release observed for 1 and 10 mM cases) are presented in Figure S10. The AuNS % releases (Figure S8) are 59% and 55% for 30 and 100 mM ionic strength, respectively. Comparison of these release amounts with those of the homo-dispersion cases (Figure S7) suggests that the presence of PA-SWNTs increases the irreversible attachment of the primary particles at high

electrolyte concentrations. The mechanism of AuNS removal in hetero-dispersion cases is likely physical filtration(Jaisi et al. 2008) of PA-SWNTs with attached AuNS particles on the SWNT surfaces. Physical filtration of PA-SWNTsthrough the sand packed column has been described in the in the transport behavior of PA-SWNT homo-dispersion: section 3.4 (Figure S8).

3.6 Transport of AuNS through PA-SWNT Coated Sand

The breakthrough curves (Figure 4) of AuNS homo-dispersions through PA-SWNTs (0.02 % PA) coated sand columns simulated pre-existing SWNTs in the porous media. Average elution of AuNSs is found to be $94.4\pm4.5\%$ and $90.3\pm3.5\%$ for 1 and 10 mM NaCl, respectively. The mobility of the AuNSs decreases significantly at higher NaCl concentration, resulting in $63.6\pm1.6\%$ and $10.6\pm6.1\%$ elution under 30 and 100 mM NaCl, respectively. Comparing Figure 4 (i.e., pre-coated sand condition) with Figure 1 (i.e., uncoated sand condition) reveals that the AuNS breakthrough is strongly influenced by the presence of PA-SWNTs on the sand grains. Average % elution is lower for the pre-coated surfaces, but thisinfluence is minor at low ionic strength. However, at 100 mM NaCl thesedifferences are profound, resulting in only $10.6\pm6.1\%$ of elution of the AuNSs through the pre-coated sand compared to $40.0\pm2.3\%$ through uncoated sand. Increased filtration of AuNSs through PA-SWNT coated sand surfaces supports the earlier hypothesis regarding preferential attachment of the AuNSs onto the PA-SWNTs. AuNSs prefer the PA-SWNT coated sand surfaces to the bare sand surfaces and thus exhibit higher filtration for the pre-coated case. Similar enhanced filtration has been reported earlier for preferential attachment of biological particles (i.e., *E. coli*) with CNTs in high electrolyte concentration(Yang et al. 2013a).

3.7 Role of NOM on AuNS Transport

The effect of NOM on AuNS transport was investigated for the AuNS homo-dispersion case through PA-SWNT coated sand at ionic strength relevant to fresh water conditions. The presence of SRHA (2.5 mg/L) shows minor enhancement in AuNS transport at 10 mM ionic strength (Figure 5); i.e., $91 \pm 3.25\%$ and $83.5 \pm 2.5\%$ AuNS elution with and without SRHA, respectively. Low average molecular weight (MW) of SRHA [~ 1490 Da (Wang et al. 2001)] in comparison to both polymers (i.e., $MW > 5000$ Da) suggests that replacement of adsorbed macromolecules by SRHA is highly unlikely (Afrooz et al. 2013a), hence had little influence on particle-particle or particle-collector interaction. Therefore, a slight increase in elution with SRHA thus is probably resulted from SRHA adsorption onto the collector surfaces (Wei et al. 2014) resulting in increased electrostatic repulsion, hence decreased filtration (Wang et al. 2015). It should be noted here that the effect of NOM on the transport of hetero-dispersion of AuNS-PA-SWNT has not been investigated in this study: SRHA is known to facilitate transport (Hyung and Kim 2008, Jaisi et al. 2008, Yang et al. 2013b), which is already very high for the hetero-dispersion cases, thus might not show significant differences.

4. Conclusions

Interaction and transport of a primary ENM (e.g., AuNS) upon environmental release with a secondary ENM (e.g., PA-SWNTs) is highly likely. Such interactions may occur while the secondary particles are in suspension (co-transport) or are already deposited onto the porous media (the collector surfaces are pre-coated). This study assesses both scenarios of filtration in presence of 1, 10, 30, and 100 mM NaCl conditions. The results indicate the following:

- The presence of PA-SWNTs does not significantly alter filtration behavior of AuNSs at low ionic strength (equivalent to fresh pore-water conditions), AuNSs are significantly more mobile and thus will travel further in the porous media at elevated ionic strengths (e.g., in saline pore-water environment) when secondary particles (e.g., PA-SWNTs) coexist with the primary ones in the pore water.
- Increased mobility of AuNSs in the presence of PA-SWNTs can be attributed to the facilitated transport of AuNSs; i.e., highly mobile PA-SWNTs act as carriers of the AuNSs.
- The pre-deposited SWNTs onto porous media will likely enhance filtration of AuNS at both low and high ionic strength conditions via facilitated removal.
- Experimental results estimate that transport distances (using CFT) of 0.1% AuNS (i.e., $C/C_0 = 0.001$) at 100 mM NaCl in homo-dispersion, hetero-dispersion, and pre-coated (with PA-SWNTs) are 0.6, 10.2, and 0.2 m respectively (Table S4), which signifies rather enhanced transport of the primary particulates in hetero-transport conditions.
- At fresh pore-water condition, the presence of NOM does not have any significant influence on co-transport of AuNSs.

In reality, however, all of these influences may become far more convoluted due to the added complexity of natural colloids and geo-macromolecules. ENM surface coatings and subsequent ligand exchange will also influence the transport behavior significantly. This is one of the first studies reporting co-transport of ENMs through porous media, and it highlights the importance of further research on such binary particulate conditions.

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List of Figure Captions:

FIGURE 1. Transport of AuNS homo-dispersion. a) breakthrough and b) % elution. 4 PV of 12.5 mg/L AuNS pulses were injected through the sand packed column at a flow velocity of 12 cm/h. The error bars represent 1 standard deviation between measured values.

FIGURE 2. Transport of PA-SWNT homo-dispersion at 100 mM NaCl as a function of PA surface modification. a) breakthrough profiles and b) % elution. 4 PV of 10 mg/L PA-SWNT pulses were injected through the sand packed column at a flow velocity of 12 cm/h. The error bars represent 1 standard deviation between measured values.

FIGURE 3. Transport of AuNS- SWNT hetero-dispersions. a) breakthrough and b) % elution. 4 PV of hetero-dispersion, i.e., 12.5 mg/L AuNS and 2.5 mg/L PA-SWNT pulses were injected through the sand packed column at a flow velocity of 12 cm/h. The error bars represent 1 standard deviation between measured values.

FIGURE 4. Transport of AuNS homo-dispersion through SWNT-coated sand column. a) breakthrough curves and b) percent transport. A 4 PV of AuNS (12.5 mg/L) pulse was injected through the PA-SWNT coated sand column at 12 cm/h of flow velocity. An equal volume of pulse of 2.5 mg/L PA-SWNT (0.02% PA) suspension was used for coating the sand at the same flow velocity. The error bars represent 1 standard deviation between measured values.

FIGURE 5. Transport of AuNS homo-dispersion through SWNT-coated sand column at 10 mM (7 mM NaCl+ 0.75 mM CaCl₂) ionic strength and with and without the presence of 2.5 mg/L SRHA. a) breakthrough curves and b) % elution. Sand was coated with a 4 PV pulse of 2.5 mg/L PA-SWNT (0.02% PA). Following this step, 4 PV pulse of 12.5 mg/L AuNS with and without SRHA were injected through the pre-coated sand. The flow velocity for all cases was 12 cm/h. The error bars represent 1 standard deviation between measured values.

Graphical Abstract:

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