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Carboxymethylcellulose Mediates the Transport of Carbon Nanotube—Magnetite Nanohybrid Aggregates in Water-Saturated Porous Media

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Abstract

Carbon—metal oxide nanohybrids (NHs) are increasingly recognized as the next-generation, promising group of nanomaterials for solving emerging environmental issues and challenges. This research, for the first time, systematically explored the transport and retention of carbon nanotube—magnetite (CNT-Fe₃O₄) NH aggregates in water-saturated porous media under environmentally relevant conditions. A macromolecule modifier, carboxymethylcellulose (CMC), was employed to stabilize the NHs. Our results show that transport of the magnetic CNT-Fe₃O₄ NHs was lower than that of nonmagnetic CNT due to larger hydrodynamic sizes of NHs (induced by magnetic attraction) and size-dependent retention in porous media. Classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory can explain the mobility of NHs under varying experimental conditions. However, in contrast with colloid filtration theory, a novel transport feature—an initial lower and a following sharp—higher peaks occurred frequently in the NHs' breakthrough curves. The magnitude and location of both transport peaks varied with different experimental conditions, due to the interplay between variability of fluid viscosity and size-selective retention of the NHs. Promisingly, the estimated maximum transport distance of NHs ranged between ~0.38 and 46 m, supporting the feasibility of employing the magnetically recyclable CNT-Fe₃O₄ NHs for in situ nanoremediation of contaminated soil, aquifer, and groundwater.

Graphical Abstract

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Introduction

Nanoscience and nanotechnology are advancing our broad societal goals in various fields including but not limited to medicine (e.g., magnetic resonance imaging),(1) agriculture (e.g., nutrient nanocapsules and nanosensors),(2) energy (e.g., solar cells and supercapacitors),(3) and environmental remediation (e.g., photocatalysts).(4, 5) They are unprecedentedly maximizing human potentials toward many frontiers such as addressing the water–energy–agriculture–environment (WEAE) nexus.(6) Recently, the focus of interest in nanomaterial (NM) research and development has shifted from singular NMs to multicomponent nanohybrids (NHs), which are nano/hierarchical assemblies of multiple NMs conjugated by noncovalent (hydrogen bond, van der Waals (vdW), and electrostatic interactions) or covalent (molecular linkage) bonds.(7–9) The goal of developing NHs is to maximize the existing functionality (e.g., contaminant adsorption and degradation efficiency) and achieve novel functionality that cannot be obtained by manipulating the singular NM system.(7–9) Taking environmental remediation as an example, the carbon nanotube (CNT) individually shows limited adsorption capacity toward metoprolol. When heterohybridized with nanoscale zerovalent iron (nZVI), the conjugated CNT–nZVI NHs exhibit significantly higher and faster adsorption and degradation efficiency for metoprolol (compared to CNT) due to a greater specific surface area (SSA) and Fenton-type catalytic reactions in the CNT–nZVI nanostructures.(10) Promisingly, compared to the single-component NMs, the performance and functionality of NHs are optimized. This is particularly true for carbon-family-based metal oxide NHs. Specifically, the photoelectrocatalytic reactivity and sensitivity of CNT/graphene oxide (GO)— $\text{Fe}_x\text{O}_y/\text{TiO}_2/\text{ZnO}/\text{MnO}_2/\text{SiO}_2/\text{Ag}$ for removing toxic gases (NO_x),(11) organic pollutants (dyes and phenolic compounds),(10, 12) heavy metals (As(III)/As(V) , Cd^{2+} , Cr(VI) , Pb^{2+} , and Hg^{2+}), (12, 13) and radionuclides (U(VI))(14, 15) are demonstrated to be greater than those of singular NMs. This is attributed to the combinative/synergistic effects within the hybridized nanostructure system.(7–9)

The superior performance and multifunctionality of carbon—metal oxide NHs make them the next-generation, promising candidates for in situ nanoremediation of contaminated air, soil, aquifer, and groundwater. It is also anticipated that increasing production and use of NHs will result in their release to the environment. However, to date, little is known about

their fate and transport in the subsurface, which will likely restrict their widespread applications in resolving issues and meeting challenges within WEAE nexus. Over the past decade, the fate and transport of individual NMs such as carbonaceous (CNT(16–19) and graphene(20–22)) and iron-bearing NMs (nZVI(23–25) and magnetite (Fe_3O_4)(26, 27)) in the subsurface have been well explored. It is noted that colloid science principles, Derjaguin–Landau–Verwey–Overbeek (DLVO) theory(28, 29) and colloid filtration theory (CFT),(30) can describe the colloidal stability and transport of individual NMs in aquatic environments. Nonetheless, deviations between experimental observations and theoretical predictions occur frequently under unfavorable attachment conditions or with varying properties (e.g., irregular shapes and surface modifications) of NMs. For example, under unfavorable conditions, nonexponential retention(31) of NMs was frequently encountered in porous media (e.g., hyperexponential retention for tubular CNT).(16) Surface modifications(32) due to surfactant and polyelectrolyte coatings impart non-DLVO interactions (steric hindrance) and change the rheological properties (viscosity) of fluid in porous media,(33) likely yielding unanticipated transport behaviors for NMs. CFT predicts that transport of colloids in porous media is controlled by random Brownian motion and that interception and gravitational sedimentation start to dominate colloid deposition when the particle diameter is $\geq 1 \mu\text{m}$.(30, 34) Once released to the environment, the transport of individual NMs is dependent on the interplay of various physicochemical conditions including (1) NM-specific properties (e.g., size/shape/hydrophilicity/aggregation state/surface chemistry), (2) medium-specific properties (e.g., grain size/shape/surface chemistry/moisture content), (3) solution chemistries (e.g., pH/ionic strength and composition (IS and IC)/presence of natural organic matter (NOM)), and (4) hydrodynamic conditions (e.g., flow rate/temperature/oxygen content).(35, 36) However, it is unclear whether the colloid science principles used for describing the environmental behaviors of individual NMs hold true for the assembled NHs, e.g., how and to what extent (e.g., qualitatively, semiquantitatively, or quantitatively) the DLVO theory and CFT explain NHs' transport in the subsurface. In particular, NHs' new features such as altered hydrophilicity, magnetism, DLVO-type (e.g., vdW attraction) interactions, and enhanced population heterogeneity (e.g., size distribution, morphology, surface defect and roughness, and charge heterogeneity; compared to individual NMs) likely impact their aggregation and transport propensities in the subsurface. (9, 37)

Assembling magnetic iron oxide (e.g., Fe_3O_4) NMs having high redox potential and contaminant immobilization capacity(38–40) with CNT having superlative mechanical strength and large SSA(41) provides a powerful strategy (e.g., synergistic adsorption and redox degradation) for in situ capturing and decomposing/detoxifying both inorganic and organic pollutants. This study systematically investigated the transport of the multifunctional CNT– Fe_3O_4 NHs in water-saturated porous media under environmentally relevant conditions. An environmentally friendly and “green” (nontoxic and biodegradable) macromolecule carboxymethylcellulose (CMC) was employed to stabilize the CNT– Fe_3O_4 NHs as they were highly hydrophobic and easily aggregated. The CMC has long been used to stabilize individual nZVI(23, 42, 43) and Fe_3O_4 NMs(44) by imparting electrosteric repulsions arising from the hydrophilic, negatively charged carboxymethyl ($-\text{CH}_2-\text{COOH}$) groups. Critical parameters characterizing the NHs' mobility in water-saturated porous

media were evaluated to shed light on the feasibility of using the recyclable CNT-Fe₃O₄ NHs for in situ nanoremediation of contaminated sites. DLVO theory and CFT were employed in combination with electrokinetic property and hydrodynamic size of NHs to understand the mechanisms behind their transport and retention within the porous media. Significant efforts were devoted to explore how DLVO theory and CFT explain the variability in NHs' transport under varying experimental conditions. Finally, potential limitations and future research directions of DLVO theory/CFT in describing NHs' transport in the subsurface were also discussed.

Materials and Methods

Preparation of CNT-Fe₃O₄ NH Influent and Solution Chemistries

Carbon nanotube (purity > 99.9%, outer diameter = 8–15 nm, inside diameter = 3–5 nm, length = 10–50 μ m, and carboxyl group content = 1.85%) was purchased from the Cheap Tubes Inc. (Grafton, VT). The CNT-Fe₃O₄ NHs were synthesized in house, and their physicochemical properties including those of purchased CNT were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, and thermogravimetric analysis (TGA) (see Supporting Information (SI) S1). The synthesized CNT-Fe₃O₄ NHs were highly hydrophobic because most hydrophilic carboxyl groups on the CNT surfaces were used for anchoring CNT and magnetite during synthesis.

The NHs were easily aggregated due to strong vdW and magnetic attractions (magnetism was confirmed using a magnet). Various surfactants (sodium dodecyl sulfate (SDS), Triton X-100, and Tween 20), polyelectrolytes (poly(acrylic acid) (PAA), poly(vinyl alcohol) (PVA), polyvinylpyrrolidone (PVP)), and macromolecules (CMC; nominal molecular weight = 90 000 g/mol; Sigma-Aldrich) were tested to investigate the NHs' colloidal stability. By monitoring the UV-vis response of absorbance for the NHs under different surfactants, polyelectrolytes, and macromolecules, we found that only the CMC at a concentration of 2% well stabilized the NHs (see SI S2). Consequently, 2% CMC was chosen as the “modifier” to stabilize the CNT-Fe₃O₄ NHs for column experiments (described below).

Environmentally relevant solution chemistries were selected to evaluate the mobility of CNT-Fe₃O₄ NHs in porous media including monovalent (0, 1, 10, and 50 mM NaCl) and divalent electrolytes (0, 0.33, 1.67, and 3.33 mM CaCl₂; note IS of 0, 0.33, 1.67, and 3.33 mM CaCl₂ is 0, 1, 5, and 10 mM, respectively), the presence of NOMs (0, 1, and 10 mg C/L Suwannee River humic acid (SRHA) and fulvic acid (SRFA)) (details on preparing SRHA/SRFA stock suspensions were given in SI S3), pHs (4.0, 7.3, and 10), and particle concentrations (10, 25, and 50 mg/L) (Table 1).⁽⁴⁵⁾ Two percent CMC-stabilized CNT-Fe₃O₄ NH influents (via adding a predetermined volume of 5% CMC stock suspension; S3) at the desired solution chemistries were freshly prepared via ultrasonication at 100 W and 42 kHz for 1 h (Branson 3510R-DTH sonicator). Changes in concentration and average hydrodynamic radius (r_h) of CNT-Fe₃O₄ NHs in the influent suspensions were monitored over the time frame of influent injection experiments (described below) to investigate their colloidal stability (aggregation propensity). The influent concentration changes of NHs were determined spectrophotometrically at 218 nm (SI Figure S1). Time-resolved dynamic light scattering (DLS) was used to monitor the r_h change of NHs in influents using the Zetasizer

Nano-ZS ZEN3600 analyzer (Malvern Instruments Inc.) at a scattering angle of 173° and 25 °C (see SI S4).

Porous Media

Ottawa sands (U.S. Silica, Berkeley Springs, WV) were chosen as representative aquifer materials for column experiments. The sands were presifted through 40, 50, 60, and 70 mesh sieves (U.S. Standard Testing Sieves), and the fractions captured by 40–50, 50–60, and 60–70 mesh sieves (average grain sizes of 360, 280, and 230 μm , respectively) were used. Before use, the sieved sands were cleaned using 1 M HCl and washed thoroughly with deionized (DI) water (Nanopure Diamond D11911, Barnstead International, Dubuque, IA). The colloidal particles from pulverized, cleaned sands were used as surrogates of sand grains for electrophoretic mobility (EPM) measurements in triplicate on the Zetasizer analyzer at 25 °C. Experimentally determined EPM values were converted to apparent zeta (ζ) potentials for the sand grains using the Smoluchowski equation.(46)

Column Experiments

Column experiments were conducted using glass chromatography columns (1.7 cm i.d. $\times$ 10 cm long).(47) Each column was dry packed using the cleaned 360, 280, or 230 μm sands. The packed column was then purged with CO_2 gas to remove any air remaining during column packing processes and to maximize the water accessibility of the column. After purging, the column was immediately saturated with DI water slowly in an upward mode. Following the saturation step, a nonreactive tracer experiment was performed to assess the hydrodynamic properties of column (see SI S5 and Table S1).

After completion of the tracer experiment, the column was pre-equilibrated with the desired background solution (Table 1). Two percent CMC was not coinjected during the pre-equilibration procedure because CMC alters the column hydromechanical (rheological) properties due to its high viscosity(33) (described below). A two-step transport experiment was then initiated by injecting 3 PVs of CNT– Fe_3O_4 NH influents (in 2% CMC) at the desired solution chemistries (designated as phase 1), followed by elution with 7 PVs of NH-free background electrolyte solution (without CMC; phase 2). Column experiments with different collector sizes (360, 280, and 230 μm , respectively) were also performed to examine the role of straining(48, 49) on NHs' retention. Previous studies suggest that, under unfavorable conditions, secondary minimum starts to capture colloids when solution IS is 10 mM NaCl(50) or 1 mM CaCl_2 .(45) To identify whether secondary minimum is also involved in NHs' retention, two three-step transport experiments were run at the highest NaCl (50 mM) and CaCl_2 concentrations (3.33 mM) investigated in this study, i.e., eluting the column with 8 PVs of DI water in phase 3 after completing the two-step transport experiments. Darcy velocity was maintained at 0.44 cm/min for all experiments, mimicking typical fluid velocities in coarse aquifers(51) or in forced gradient in situ remediation.(52) Column effluents were collected via a fraction collector. Following completion of each transport experiment, the spatial distribution of CNT– Fe_3O_4 NHs retained in the column (dissection experiments) was determined (SI S6). Column transport and dissection experiments were also performed for CNT alone (in 2% CMC) to compare the mobility between NHs and parent NMs.

The concentrations of CNT-Fe₃O₄ NHs and CNT in the effluents and retentates (retained colloids collected from dissection experiments) were determined spectrophotometrically at 218 nm (SI Figure S1). To eliminate the interferences of CMC in NHs (and CNT) measurements, two-step column transport experiments were also performed for 2% CMC alone under experimental conditions identical to those for the transport of CNT-Fe₃O₄ NHs (Table 1). The actual concentration of CNT-Fe₃O₄ NHs (and CNT) in the effluents was obtained by subtracting the spectrophotometric response (at 218 nm) of CMC from that of the NHs (and CNT) at the identical PV. Furthermore, to minimize the potential interferences of particle aggregation and sedimentation, spectrophotometric measurements for all NHs, CNT, and CMC in the effluents were controlled to be completed within 1.5 h after collecting from the fraction collector. Additionally, selected column effluents of NHs were digested in 2.6 M HNO₃ for 3 days at 25 °C and then filtered through 0.2 µm cellulose acetate membranes. Total Fe concentrations in the filtered digestion solutions were determined using inductively coupled-plasma optical emission spectroscopy (ICP-OES; PerkinElmer Optima 3300DV, Norwalk, CT) to verify the reliability of spectrophotometric measurements of the NHs. Selected column effluents of NHs were also measured using ICP-OES (effluents after HNO₃ digestion for total Fe measurements) to identify whether Fe₃O₄ NMs detach from the NHs or dissolve under acidic conditions (pH 4.0). Our measurements (Fe content < detection limit, meaning no Fe₃O₄ NMs detach or dissolve) substantiate the integrity of the NHs during porous media transport.

Electrokinetic Properties and Hydrodynamic Radii of CNT-Fe₃O₄ NHs in the Influent

Electrophoretic mobility (EPM) and ζ-potential of CNT-Fe₃O₄ NHs (and CNT) in various influents (Table 1) were measured using the Zetasizer analyzer at 25 °C. The ζ-potentials of CNT-Fe₃O₄ NHs and sand grains were then used to calculate their interaction energy using DLVO theory that includes vdW and electrostatic double-layer (EDL) interactions. It is impossible to determine Hamaker constant (*A*) of the hydrophobic CNT-Fe₃O₄ NHs (without CMC modification) in aqueous solutions experimentally. Thus, three Hamaker constants, i.e., Hamaker constants of CNT ($A_{\text{CNT}} = 6.00 \times 10^{-20}$ J)(53, 54) and Fe₃O₄ NMs ($A_{\text{Fe}_3\text{O}_4} = 33.0 \times 10^{-20}$ J)(55) and an estimated Hamaker constant of the NHs ($A_{\text{CNT-Fe}_3\text{O}_4} = 17.6 \times 10^{-20}$ J) based on the Hamaker constants of parent NMs and NHs' elemental (C and Fe) contents, were employed to calculate the interaction energy between NHs and sand grains.(56, 57) Details on the DLVO interaction energy calculation including the inherent limitation of this approach are given in SI S7.

The average hydrodynamic radius (*r_h*) of CNT-Fe₃O₄ NHs (and CNT) in various influents and the hydrodynamic particle size distribution of CNT-Fe₃O₄ NHs in the influents at different NaCl and CaCl₂ concentrations were determined using DLS (described above). Particle size distribution of 2% CMC was also determined to investigate the role of CMC on the transport of CNT-Fe₃O₄ NHs. The CONTIN algorithm was used to convert intensity autocorrelation functions to intensity-weighted *r_h* using the Stokes–Einstein equation for spherical particles.(58) Given that the NHs, CNT, and CMC are nonspherical, DLS provides the diameter of a sphere that has the same average translational diffusion coefficient as the particle being measured. For selected column experiments, the *r_h* of NHs and CNT in the

effluents and retentates (retained in the column inlet 0–1 cm) was measured using DLS to understand size-dependent retention in saturated sand.

Data Analyses

Parameters characterizing the mobility of CNT–Fe₃O₄ NHs in water-saturated porous media including single-collector contact efficiency (η), attachment efficiency (α), deposition rate coefficient (k_d), and maximum transport distance ($L_{\max}$) were calculated using the well-defined Tufenkji–Elimelech (TE) equation (SI S8).(34)

Results and Discussion

Electrokinetic Properties and Hydrodynamic Radii of CNT–Fe₃O₄ NHs in the Influent and Electrokinetic Properties of Sand Grains

Physicochemical properties of CNT–Fe₃O₄ NHs and CNT were characterized using XRD, TEM, Raman spectroscopy, and TGA (Figure 1). A strong peak occurred at 26.5° for both NHs and CNT in the XRD spectra, which corresponds to the d spacing of the [002] plane of graphite (CNT; Figure 1a).(59) In contrast, the characteristic reflections of 30.0° [220], 35.6° [311], and 43.4° [400] of Fe₃O₄ (JCPDS No. 19–0629) occurred only for the NHs, confirming the successful hybridization of CNT and Fe₃O₄ NMs. TEM images showed that the Fe₃O₄ NMs (20–30 nm size) heterogeneously deposited on CNT's surface as dense aggregates (Figure 1b). This is due to the large SSA and surface reactivity and strong magnetic attraction of the Fe₃O₄ NMs that promote partial aggregation on the CNT's surface (see SI Figure S5). The Fe₃O₄ NMs were strongly anchored on the CNT's surface even after ultrasonication treatment (100 W and 42 kHz for 1 h) since no Fe was released from the NHs (via ICP-OES measurements). This could be due to the strong covalent interaction between CNT (e.g., carboxyl (1.85% in the pristine CNT) and carbonyl groups) and Fe₃O₄ NMs.(7) The Raman spectrum of CNT exhibited three absorption bands at 1343, 1571, and 2688 cm^{−1} (Figure 1c), which are assigned to the D, G', and G' bands, respectively.(60) However, these three bands shifted to higher wavenumbers of 1357, 1582, and 2710 cm^{−1}, respectively, for the NHs, yielding a larger D/G-band intensity ratio of $I_D/I_G = 0.326$ ($I_D/I_G = 0.316$ for CNT). This indicates a smaller average size of the sp² domains of carbon for the NHs,(60) likely due to the enhanced aggregation of NHs (more compressed structure) induced by magnetic attraction (see S1 for more discussion). The TGA profiles showed that Fe accounted for 42.8% of the total elemental mass because CNT was decomposed completely when the temperature was >930 °C (Figure 1d). The C and Fe elemental composition information was used to calculate the Hamaker constant and density of the NHs for DLVO interaction energy and transport parameter calculations (described below).

The EPMs and ζ -potentials of CNT–Fe₃O₄ NHs in the influents (in 2% CMC) and sand grains under different experimental conditions are shown in Table S2. Both NHs and sand grains were negatively charged, suggesting unfavorable conditions for column experiments. As mentioned above, the NHs without CMC modification were highly hydrophobic, making EPM (and DLS) measurements impossible in aqueous solutions. However, in 2% CMC, the ζ -potentials of NHs in the influents were highly negative (−39.4 to −58.7 mV) due mainly to the adsorption of hydrophilic, negatively charged carboxymethyl groups of CMC (e.g., ζ -

potential of 2% CMC alone = -49.3 mV at 1 mM NaCl and pH 7.3) onto NHs' surface. The ζ -potential of NHs in the influents (in 2% CMC) was more negative than that of 2% CMC alone at a specified solution chemistry, e.g., $-53.4 > -49.3$ mV at 1 mM NaCl and pH 7.3 (Table S2). This discrepancy could be due to the deprotonation of carboxyl and carbonyl groups of the NHs, although most carboxyl groups are expected to be used for anchoring CNT and magnetite NMs (described above). Consistent with reported results for individual NMs and sand grains,(61–63) decreasing IS and increasing NOM concentration and pH increased (more negative) the ζ -potential of both NHs and sand grains. The divalent Ca^{2+} decreased the ζ -potentials of NHs and sand grains more than monovalent Na^+ at equivalent ISs by greater charge screening (both Na^+ and Ca^{2+}) and neutralization (Ca^{2+} only) effects. (46)

Table S2 also shows the variability in η_h of CNT- Fe_3O_4 NHs in the influents (2% CMC) with varying experimental conditions. Greater aggregation (larger η_h) of the NHs was associated with the lower ζ -potentials due to less electrostatic repulsions according to the DLVO interaction prediction (described below). Similar findings have been documented for individual NMs.(61, 62) The measured hydrodynamic diameter ($2\eta_h$) of NHs and CNT (Table S2) lied within the diameter (8–15 nm) and length (10–50 μm) of the CNT, consistent with the results reported previously.(19) This is likely because, for nonspherical NHs and CNT, DLS gives the diameter of a sphere that has the same average translational diffusion coefficient as the particle (NHs and CNT) being measured (described above).

Mobility Comparison between CNT- Fe_3O_4 NHs and Individual CNT

Breakthrough curves (BTCs) and retention profiles (RPs) of CNT- Fe_3O_4 NHs and CNT (both in 2% CMC) under the identical transport condition (1 mM NaCl and pH 7.3) are presented in Figure 2. Total mass recoveries (M_{tot}) of NHs in the effluents (M_{eff}) and retentates (M_{ret}) under different experimental conditions are given in Table 1, which confirms a high degree of confidence in our experimental measurements because virtually all NHs were recovered from column experiments ($M_{\text{tot-NHs}} = 93.5\text{--}108\%$ and $M_{\text{tot-CNT}} = 99.4\%$). The ICP-OES results for effluent Fe analyses matched (standard errors $< 5\%$) the NHs' BTC data, further demonstrating the reliability of the UV-vis spectrophotometric method for the NHs' quantification. No physical nonequilibrium processes(64) occurred in the column because of the symmetrical and no-tailing BTC of the tracer (S4) with the exception of the one in 230- μm sand (described below).

The mobility of CNT- Fe_3O_4 NHs was lower than that of CNT with less transport ($M_{\text{eff}} = 79.9\%$ vs 95.1%) and greater retention ($M_{\text{ret}} = 25.0\%$ vs 4.3%) (Figure 2a and 2b). Interestingly, transport of both NHs and CNT reached a lower peak initially (at 1.5 PV) and maintained the peak plateau for 2 PVs (designated as “peak 1”) and then increased sharply to achieve the second higher peak (“peak 2”) upon switching background electrolyte solution (without CMC) into the column (at 3 PV; Figure 2a). The two-peak transport feature has never been reported previously and is anticipated to be associated with the transport behavior of the “modifier”—CMC. The BTC of 2% CMC alone at the identical transport condition is shown in Figure 2c, which replicated the transport characteristics of NHs/CNT with two transport peaks and long-term tailings. While previous studies

frequently employed CMC to stabilize individual NMs, the impact of CMC on the transport behavior of NMs was insignificant due to the low applied CMC concentrations (1%). The observed two-peak transport feature of 2% CMC (and NHs and CNT) is due primarily to the viscosity difference between CMC and water. Specifically, the viscosity of CMC (90 000 g/mol) is at least 2 orders of magnitude higher than that of water (~300 vs 0.89 mPa.s at 25 °C),⁽³³⁾ so the transport velocity of CMC is much lower than that of water in porous media (higher viscosity, lower transport velocity), which explains the sharp peak 2 and long-term tailing of CMC when replacing CMC with water (at 3 PV). The early breakthrough (peak 1) of CMC indicates that heterogeneity occurred in the CMC populations that exhibited varying transport velocities. Indeed, heterogeneities in molecular weight and crystallite,⁽⁶⁵⁾ configuration,⁽⁶⁶⁾ aggregation state,⁽³³⁾ and particle size are expected to affect the rheological property (Newtonian behavior) and thus transport velocity of CMC (see SI S9 for more discussion). The hydrodynamic particle size distribution of 2% CMC (1 mM NaCl and pH 7.3) is presented in SI Figure S4b, which shows the size heterogeneity in the CMC populations: 36.2% (area 1) and 63.8% (area 2) CMC particles have sizes of 0.40 ± 0.11 and 4.6 ± 1.4 nm, respectively. The smaller CMC particles having lower viscosity are likely to breakthrough earlier, yielding peak 1. Nonetheless, most CMC particles have high viscosity (greater than that of water), and thus, most CMCs exhibit more retarded breakthrough (peak 2). Clearly, the early breakthrough and long-term tailing of 2% CMC alone suggest viscosity heterogeneity among CMC populations.

The transport pattern of both NHs and CNT replicated the breakthrough behavior of CMC, highlighting CMC-mediated transport of NHs/CNT. The normalized effluent values (C/C_0) of both peaks and peak locations of the peak 2 varied with different degrees of tailing. Specifically, the C/C_0 values of both peaks followed the identical order NHs < CNT < CMC (Figure 2a and 2c), which is opposite to the order of their r_h values in the influents ($1632 > 1526 > 3.4$ nm) (Table S2 and Figure S4). This is due primarily to the greater interception efficiency (η_I) and overall single-collector contact efficiency (η_o) at larger r_h , because η_I and η_o increase monotonically with colloid size when the diameter is $> 1 \mu\text{m}$.⁽³⁴⁾ To better understand the two-peak transport feature, r_h of NHs and CNT in the influents, effluents, and retentates was determined (Figure 2d and Table 2). The r_h of NHs was in the order effluent < influent < retentate (e.g., $1432 < 1632 < 2001$ nm in 1 mM NaCl and pH 7.3; Table 2), indicating size-selective retention in porous media. The size-selective retention that larger particles preferentially retain in the column (retentates) due likely to greater η_I and η_o and smaller ones elute out (effluents) has been reported in colloid transport studies.⁽⁴⁷⁾ Furthermore, for the effluents, the r_h of both NHs and CNT increased progressively with PV (Figure 2d), again strongly substantiating the size-selective retention. It is thus logical to anticipate that smaller NHs/CNT associated with lower viscous CMCs breakthrough earlier (yielding peak 1), whereas larger NHs/CNT coated with higher viscous CMCs are eluted out more retarded (i.e., peak 2). The peak location of peak 2 was earlier for CNT than that of NHs (4.5 vs 5 PV; Figure 2a), further supporting that larger cumbersome NHs (effluent r_h : CNT < NHs; Figure 2d) have a lower transport velocity (i.e., more retarded breakthrough). Greater retention of NHs observed in Figure 2b is due to greater r_h (greater η_I and η_o) in the influents and effluents (Figure 2d). In summary, the above results underscore the interplay of

viscosity variability of fluid and size-selective retention in the transport of NMs (in 2% CMC) in water-saturated porous media.

Mobility of CNT–Fe₃O₄ NHs under Varying Physicochemical Conditions

Environmentally relevant physicochemical conditions were chosen to investigate the mobility of CNT–Fe₃O₄ NHs (in 2% CMC) including NaCl (Figure 3a and 3b), CaCl₂ (Figure 3c and 3d), SRHA (Figure 3e and 3f), and SRFA concentrations (Figure 3g and 3h), pHs (Figure S6a and S6b), particle concentrations (Figure S6c and S6d), and collector sizes (Figure S6e and S6f). The DLVO interaction energies between CNT–Fe₃O₄ NHs and sand grains under different experimental conditions are shown in SI Figure S7 and Table S3. Before interpreting the mobility of NHs under different experimental conditions, it is important to understand the colloidal stability of NH influents. In 2% CMC, the NH influents were stable (influent concentration and η_h stayed unchanged; Figure S2) over the time frame of influent injection experiments. Recalling that without CMC partial aggregation of NHs was pronounced due to magnetic attraction (Figure S5), our findings emphasize the critical role of 2% CMC in stabilizing the NH aggregates (e.g., NHs exist as stable aggregates because η_h varies with solution chemistries). No further aggregation and gravitational sedimentation of NHs occurred in the influents during influent injection experiments, again confirming the strong stabilizing effect of 2% CMC. Nonetheless, both CFT and TE equation predict that gravitational sedimentation is appreciable when colloid diameter is $\sim 1\ \mu\text{m}$. (30, 34) This is likely because highly viscous and negatively charged CMCs (described above) counterbalance the role of gravity in causing particle sedimentation.

Similarly, the two-peak transport feature occurred frequently in the NHs' BTCs with altered C/C_0 values and peak locations (Figures 3 and S6). Decreasing IS and increasing NOM concentration, pH, particle concentration, and collector size (with the exception of 230 μm sand; Figure S6e and S6f) increased the mobility of NHs (see M_{eff} and M_{ret} in Table 1), consistent with DLVO theory prediction (Figure S7 and Table S3). The lower mobility of NHs under different experimental conditions was again associated with less negative ζ -potential and larger η_h due to greater η_l and η_o . The size-selective retention also occurred during NHs transport (η_h order effluent < influent < retentate; Table 2), and this effect became more pronounced (increased η_h) at higher NaCl/CaCl₂ concentrations. To better unravel the size-selective retention of NHs in porous media, the hydrodynamic particle size distribution of NHs in the influents (in 2% CMC) was determined (SI Figure S8). Our results indicate a greater degree of particle size heterogeneity (wider particle size distribution) among NHs populations, likely accounting for the greater size-selective retention of NHs at higher NaCl/CaCl₂ concentrations. Other potential explanations for the greater size-selective retention at higher NaCl/CaCl₂ concentrations include deeper attractive secondary minimum (Table S3) and more pronounced straining (Table 2) given that hyperexponential RPs occurred at high NaCl/CaCl₂ concentrations (Figure 3b and 3d). The fact that retained NHs were released upon injecting DI water during the three-step transport experiments (SI Figure S9a) substantiates the important role of secondary minimum in NHs' retention. However, the extent of NHs' release was much less in Ca²⁺ than in Na⁺ due likely to more pronounced straining due to the larger η_h of NHs in the influents, effluents, and retentates (Table 2 and

Figure S9b), i.e., Ca^{2+} bridges the $-\text{CH}_2\text{COOH}$ and $-\text{COOH}$ groups of CMC-coated CNT- Fe_3O_4 NHs. Straining is demonstrated to play a critical role in colloid retention and cause hyperexponential RPs when the diameter ratio of colloid vs collector is 0.008.(49) Our calculations show that when the size ratio of NHs vs collector was 0.00937 (10 mM NaCl and 1.67 mM CaCl_2 ; Table 2), straining started to yield the hyperexponential RPs (Figure 3b and 3d). The slight difference ($0.008 < 0.00937$) of the threshold for straining between our and previous work(49) is due again to the strong stabilizing effect of CMC used (described above). Moreover, straining likely narrows down the pore structure due to particle retention, particularly near the column inlet, further aggravating the hyperexponential retention (e.g., at higher NaCl/ CaCl_2 concentrations).(21) Please note that while no aggregation of NHs occurred in the influents (described above), particle aggregation was observed in the column system particularly at higher ISs (see retentate vs influent size; Table 2 and Figure S8) due primarily to greater η_{I} , η_{O} , and straining within the porous media structures. The unexpected higher mobility and longer tailing in 230 μm sand compared to those in 280 and 360 μm sands (Figure S6e and S6f) are due to the higher dispersivity (0.23 vs 0.16 cm; Table S1) of the NHs in the 230 μm sand (tracer's BTC also exhibited a longer tailing; data not shown). Consistent with previous findings for individual NMs,(18, 61) the reduced retention of NHs at higher particle concentrations (Figure S6c and S6d) is owing to greater degrees of blocking of retention sites on the sand grains under unfavorable conditions (Table S3).

Variability in C/C_0 value of both peaks and shift of peak 2 location under different experimental conditions is again due to the coupling of change in fluid viscosity and size-dependent transport in porous media. For example, the C/C_0 value of peak 1 changed with solution chemistries (IS, NOM, and pH; Figures 3 and S6a and S6b), e.g., lower C/C_0 value was generally coupled with larger τ_{h} due to greater η_{I} and η_{O} . However, it stayed unchanged with varying particle concentration and collector size (Figure S6c–f) likely because particles in peak 1 (relatively smaller particles associated with lower viscous CMCs, described above) are insensitive to influent concentration and pore structure in porous media. Introducing NOM in the influent or increasing influent pH expedited the early breakthrough of peak 2 (peak location evolved from 5 to 4.5 PV; Figures 3e, 3g, and S6a) because the transport velocity of NOM is much higher than that of viscous CMC in water and that NOM (and high pH) promotes the dispersion of colloids/NMs due to electrosteric repulsion effect (see ζ -potential, τ_{h} , and DLVO interaction energy data in Tables S2 and S3). In certain cases, interestingly, peak 2 disappeared completely, e.g., at high ISs (10–50 mM NaCl and 1.67–3.33 mM CaCl_2), at low pH (4.0), and in 280 μm sand or shortened (0.33 mM CaCl_2) with limited tailing. This is mainly because the breakthrough of CMC was inhibited to a similar extent, i.e., 2% CMC alone exhibited similar BTCs (peak 1 or two peaks with shortened peak 2; data not shown) under these experimental conditions. High ISs decreased the ζ -potential (less negative) and reduced the viscosity (smaller difference in viscosity among CMC populations)(33) of CMC, yielding lower mobility of CMC with less retardation of peak 2 (or complete disappearance). These findings are again indicative of CMC-mediated transport of NHs. NOM (1–10 mg C/L; Figure 3e–g) promoting the long-distance transport of NHs as evidenced by the long-term tailing and very limited retention. Also, variability in the transient viscosity of pore–water when injecting background electrolyte in phase 2 would

influence the C/C_0 value and location of peak 2 due to the presence of free CMC in porous media, which likely alters the properties of both NHs and collectors.

Exponential and hyperexponential RPs occurred for the NHs (Figures 3 and S6), and straining was responsible for the hyperexponential RPs (described above). Very recently, Goldberg et al.(67) employed a novel decision tree method to quantitatively identify the influence of physicochemical conditions on the retention of NMs in water-saturated porous media and highlighted that high advective flows and influent concentrations masked the impact of other physicochemical conditions, yielding exponential RPs. This well explains the observed exponential RPs of NHs under different particle concentrations (Figure S6d). They also emphasized the dominant role of straining in causing hyperexponential RPs at high aspect ratios of particle vs collector.(67) This supports the critical role of straining in yielding the hyperexponential RPs at higher NaCl/CaCl₂ concentrations (larger η_h and thus higher aspect ratio of particle vs collector).

Parameters Characterizing the Mobility of CNT–Fe₃O₄ NHs

The overall single-collector contact efficiency (η_o) that reflects the contribution of individual transport mechanisms of Brownian diffusion (η_D), interception (η_I), and gravitational sedimentation (η_G) was calculated to unravel the mechanisms controlling NHs' transport and retention (Table S4). Regardless of Hamaker constant, diffusion (η_D) dominated the η_o and gravity (η_G) and interception (η_I) started to play more important roles at higher ISs or lower pHs, consistent with the trends of η_h under varying physicochemical conditions (described above). A higher Hamaker constant yielded larger η_D , η_I , η_G , and thus η_o due to a greater contribution of vdW attraction (eqs 12 and 13 in S8 S8). However, some η_o values were determined to be 1.0, especially when using the highest Hamaker constant of $A_{Fe_3O_4} = 33.0 \times 10^{-20}$ J for the calculation, which is inconsistent with the prediction of the TE equation.(34) Potential discrepancies in η_o between our and Tufenkji and Elimelech's work(34) are due to the larger Hamaker constants ($6.00\text{--}33.0 \times 10^{-20}$ vs $0.30\text{--}4.00 \times 10^{-20}$ J) and densities ($1.74\text{--}5.15$ vs $1.00\text{--}1.80$ g/cm³) of the CNT–Fe₃O₄ NHs and lower porosities ($0.33\text{--}0.34$ vs $0.36\text{--}0.40$) of the packed column used here. The estimated α of NHs under different experimental conditions ranged between 3.97×10^{-3} and 6.91×10^{-3} (Table S4), which is smaller than those of individual CNT ($0.05\text{--}1.0$),(19) fullerene ($0.01\text{--}1.0$),(68) and nZVI ($2.00 \times 10^{-3}\text{--}1.0$)(24) NMs for similar solution chemistries. The higher mobility of the NHs in 2% CMC (Table 1) and larger η_o of the packed columns (eq 15 in S8 for α calculation) yielded the smaller α in this study.

Figure 4 and Table S4 show the variability in k_d and L_{max} under varying physicochemical conditions. For a specified experimental condition, the calculated k_d and L_{max} values were the same, regardless of Hamaker constant, because the overall contribution of Hamaker constant was counterbalanced in the term of $\alpha\eta_o$ in eqs 16 and 17 in S8. Consequently, while the Hamaker constant of CNT–Fe₃O₄ NHs was not determined experimentally, the calculated k_d and L_{max} values were reliable. The k_d was smaller and L_{max} was larger in Na⁺ than in Ca²⁺ at the equivalent IS (1 and 10 mM; Figure 4), implying that Ca²⁺ inhibited NHs' mobility to a greater extent than that of Na⁺. The extent of k_d and L_{max} change (k_d and L_{max}) vs IS became smoother at higher ISs (both Na⁺ and Ca²⁺), likely due to the

stabilizing effect of CMC coating on NHs' surface that cushions the impact of electrolyte. Notably, $L_{\max}$ elevated significantly with environmentally relevant concentrations (10 mg C/L) of NOMs particularly for SRHA (~28 m), signifying that the NHs would be highly mobile in the subsurface rich in NOMs. Over the range of physicochemical conditions investigated, k_d and $L_{\max}$ ranged between 3.27×10^{-5} and $3.93 \times 10^{-3} \text{ s}^{-1}$ and 0.38 and 46 m, respectively, which are smaller (for k_d) and larger (for $L_{\max}$) than those previously reported for individual NMs (19, 24, 68) under similar experimental conditions due, again, to the strong stabilizing effect of CMC.

The TE equation is a well-defined semiempirical correlation equation commonly used for predicting η_D , η_I , η_G , and η_o , regardless of favorable/unfavorable conditions, and it has some assumptions. For example, the TE equation assumes spherically shaped colloids and constant viscous fluid. The CNT-Fe₃O₄ NHs used, however, were nonspherical, and fluid viscosity varied when flushing the column with background solution in column transport experiments. Thus, the TE equation calculation should be considered as estimation of anticipated changes in η_D , η_I , η_G , and η_o with varying experimental conditions and viewed as an approximation of k_d and $L_{\max}$. Future field studies should be implemented to test the applicability of the TE equation for k_d and $L_{\max}$ evaluation.

Potential Limitations of DLVO Theory and CFT in Describing NHs' Transport

DLVO theory and CFT have been used to describe the transport of colloids/NMs in porous media, but both strategies have assumptions and potential limitations. Specifically, DLVO theory calculations consider average ζ -potentials for both colloids and collector grains and assume geometrically spherical colloids. Nevertheless, the CNT-Fe₃O₄ NHs were nanoheteroaggregates of tubular CNT anchored by spherical Fe₃O₄ NMs (Figure 1b), and the measured ζ -potentials of NHs were the overall surface charges of the nanoassemblies. Moreover, the Hamaker constant of CNT-Fe₃O₄ NHs cannot be accurately quantified in aqueous solution. Thus, the DLVO calculations should be viewed as an estimation of expected changes in the average interaction energy between NHs and collectors with varying experimental conditions (Table S3). CFT predicts an exponential decrease in colloid retention with transport distance and functions satisfactorily under favorable conditions. However, deviations between experimental data and theory predictions occur under unfavorable conditions including the encountered hyperexponential RPs for CNT-Fe₃O₄ NHs. This is due primarily to the interplay of size-selective retention and straining in column systems. While NHs' transport behaviors under different experimental conditions can be described by DLVO theory/CFT semiquantitatively, future studies should focus on developing more rigorous approaches (e.g., modified DLVO theory/CFT) for quantitatively describing the transport of NHs taking into account, for example, variability of fluid viscosity and NHs' shape, morphology, magnetism, surface chemistry, and aggregation state.

Environmental Implications

Our findings provide valuable knowledge into in situ nanoremediation of contaminated soil, aquifer, and groundwater using the next-generation multifunctional carbon-metal oxide NHs. The rationale of employing the magnetically recyclable CNT-Fe₃O₄ NHs relies on the

fact that the assembled nanostructures of CNT and Fe₃O₄ have much higher SSA and reactivity (compared to singular NMs), where (in)organic pollutants can be adsorbed and then detoxicated/degraded in situ. Nonetheless, the major challenges arise from the strong hydrophobicity and magnetism of the CNT–Fe₃O₄ NHs that promote particle aggregation, which deteriorates the overall performance of material. Our results show that 2% CMC can significantly increase the CNT–Fe₃O₄ NHs' hydrophilicity, colloidal stability, and mobility in aqueous solutions, reaching the optimal transport ranges (several to dozens of meters) required for in situ remediation.(38) Other crucial benefits of utilizing the “green” and low-cost CMC include (1) the efficacy of NHs would not be compromised by the CMC coating, as demonstrated by Bhattacharjee et al.(43) in the degradation of trichloroethylene using CMC-coated nZVI, (2) no adverse impact would occur during remediation because the CMC is biodegradable, and particularly (3) CMC and its biodegraded intermediates (primarily celluloses) can act as a carbon source for microbes during microbial bioremediation, making the in situ, combined “nanoremediation–bioremediation” technology most promising. Due to the distinct viscosity of CMC and water, the transport of CMC-modified NHs to the targeted contaminant plumes would be retarded, depending on the applied CMC concentration and hydrogeological properties (e.g., flow velocity, IS, pH, and NOM) of the aquifers or groundwater. This will likely extend the operational time of in situ nanoremediation. Even if the aquifer or groundwater has a high IS of 50 mM NaCl or 3.33 mM CaCl₂, the NHs are still expected to be mobile ($L_{\max}$ = 0.43 and 0.38 m, respectively; Table S4). In particular, the $L_{\max}$ increased to ~3.7–28 m under environmentally relevant concentrations (1–10 mg C/L) of NOMs and reached up to ~46 m at a particle concentration of 50 mg/L, supporting the feasibility of employing the CNT–Fe₃O₄ NHs for in situ contaminated site remediation. Currently, the synthesis methods of CNT–metal oxide NHs are mature, as have been showcased in ref 37 (our recent book chapter). Nonetheless, the major obstacle of employing NHs for remediation purposes arises from the relatively high cost of the NHs. If the mass production of commercial inexpensive NHs is achieved, we can envision that the multifunctional NHs are highly likely to be employed as the next-generation candidates for in situ nanoremediation of contaminated sites.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. XRD patterns (a), TEM images (b), Raman spectra (c), and TGA profiles (d) of the synthesized carbon nanotube-magnetite nanohybrids (CNT-Fe₃O₄ NHs) and parent CNT component.

Figure 2.

Breakthrough curves (BTCs; a) and retention profiles (RPs; b) of CNT-Fe₃O₄ NHs and individual CNT, respectively, in water-saturated sand columns at 1 mM NaCl and pH 7.3 (in 2% CMC). Breakthrough curve describes the normalized effluent concentration of NMs, C/C_0 (where C_0 is the initial influent concentration of CNT-Fe₃O₄ NHs or CNT) as a function of pore volume (PV), and retention profile shows the normalized solid-phase retention concentration of NMs, S/C_0 (where S is retention amount of CNT-Fe₃O₄ NHs or CNT per gram dry sand) as a function of distance from the column inlet. For column transport experiments, 3 PVs (marked by dashed line in a) of CNT-Fe₃O₄ NH or CNT influent were injected in the column followed by elution with 7 PVs of NM-free background electrolyte solution (without CMC). Other column transport parameters were the same including CNT-Fe₃O₄ NH or CNT influent concentration = 10 mg/L, influent pH = 7.3, background electrolyte = 1 mM NaCl, average sand grain size = 360 μ m, and Darcy velocity = 0.44 cm/min. (c) For comparison, the breakthrough curve of 2% CMC alone under experimental conditions (1 mM NaCl and pH 7.3) identical to that of NHs/CNT is shown. (d) Average hydrodynamic radius (r_h) of CNT-Fe₃O₄ NHs and CNT in the effluents

(collected from a). Error bars represent the standard deviations from duplicate experiments. Note different y-axis scales in figure.

Figure 3.

Breakthrough curves (a, c, e, and g) and retention profiles (b, d, f, and h) of CNT-Fe₃O₄ NHs in water-saturated sand columns under different concentrations of NaCl (0, 1, 10, and 50 mM; a and b), CaCl₂ (0, 0.33, 1.67, and 3.33 mM; c and d), SRHA (0, 1, and 10 mg C/L; e and f), and SRFA (0, 1, and 10 mg C/L; g and h), respectively, in 2% CMC. Other column transport parameters include injection volumes of CNT-Fe₃O₄ NH influent = 3 PVs (marked by dashed lines in a, c, e, and g), influent concentration = 10 mg/L, influent pH = 7.3, average sand grain size = 360 μm, and Darcy velocity = 0.44 cm/min (see Table 1). Error bars represent the standard deviations from duplicate experiments.

Figure 4.

Calculated deposition rate coefficient (k_d ; left y axis) and maximum transport distance (L_{max} ; right y axis) of CNT-Fe₃O₄ NHs at varying concentrations of NaCl (0, 1, 10, and 50 mM; a), CaCl₂ (0, 0.33, 1.67, and 3.33 mM; a; note that IS of 0, 0.33, 1.67, and 3.33 mM CaCl₂ is 0, 1, 5, and 10 mM, respectively), SRHA (0, 1, and 10 mg C/L; b), and SRFA (0, 1, and 10 mg C/L; b), respectively, using the Tufenkji-Elimelech (TE) equation.⁽³⁴⁾ It is important to point out that the k_d and L_{max} values were calculated to be the same regardless of the Hamaker constants used for the calculations (see SI Table S4). Note different y-axis scales in the figure.

Table 1.

Physicochemical Properties of Column Transport Experiments and Mass Recoveries of CNT–Fe₃O₄ NHs (in 2% CMC) under Different Experimental Conditions^a

NaCl (mM)	CaCl ₂ (mM)	SRHA (mg C/L)	SRFA (mg C/L)	pH	particle conc (mg/L)	sand size (μm)	mass recovery (%)		
							M _{eff}	M _{ret}	M _{tot}
0	0	0	0	7.3	10	360	88.3 ± 0.02	12.8 ± 0.25	101 ± 0.23
1	0	0	0	7.3	10	360	79.9 ± 2.4	25.0 ± 0.49	105 ± 2.9
10	0	0	0	7.3	10	360	37.8 ± 0.67	62.2 ± 1.1	100 ± 0.41
50	0	0	0	7.3	10	360	20.3 ± 0.88	84.2 ± 0.18	104 ± 1.1
0	0.33	0	0	7.3	10	360	57.4 ± 2.0	44.2 ± 2.2	102 ± 0.29
0	1.67	0	0	7.3	10	360	22.7 ± 4.4	73.1 ± 0.9	95.8 ± 3.5
0	3.33	0	0	7.3	10	360	16.2 ± 0.84	86.9 ± 1.4	103 ± 2.3
1	0	1	0	7.3	10	360	86.9 ± 1.5	14.2 ± 0.28	101 ± 1.2
1	0	10	0	7.3	10	360	97.6 ± 3.8	8.0 ± 0.28	106 ± 4.1
1	0	0	1	7.3	10	360	83.1 ± 2.6	14.9 ± 0.72	98.0 ± 1.9
1	0	0	10	7.3	10	360	92.2 ± 1.2	9.7 ± 0.77	102 ± 0.41
1	0	0	0	4.0	10	360	35.0 ± 0.58	66.1 ± 1.8	101 ± 2.4
1	0	0	0	10	10	360	89.5 ± 0.67	16.1 ± 0.49	106 ± 1.2
0	0	0	0	7.3	25	360	98.5 ± 1.2	8.0 ± 0.36	107 ± 1.5
0	0	0	0	7.3	50	360	104 ± 0.49	4.0 ± 0.30	108 ± 0.19
1	0	0	0	7.3	10	280	28.6 ± 1.8	64.9 ± 0.89	93.5 ± 2.7
1	0	0	0	7.3	10	230	97.4 ± 0.36	6.1 ± 0.42	104 ± 0.79

^a SRHA and SRFA are Suwannee River humic acid and Suwannee River fulvic acid, respectively. Conc is concentration. M_{eff}, M_{ret}, and M_{tot} are mass percentages of CNT–Fe₃O₄ NHs recovered from effluent, retentate, and total column, respectively. Other column transport parameters such as porosity, pore–water velocity, and dispersivity are shown in SI Table S1.

Table 2.

Average Hydrodynamic Radius (r_h) of CNT-Fe₃O₄ NHs in the Influent (in 2% CMC), Effluents, and Retentates at Different NaCl and CaCl₂ Concentrations

r_h (nm)						
NaCl (mM)	CaCl ₂ (mM)	sand grain diameter (μ m)	influent	effluent ^a	retentate ^b	r_h/r_{50} (-) ^d
0	0	360	994 $\pm$ 226	836 $\pm$ 48	1096 $\pm$ 41	5.52 $\times 10^{-3}$
1	0	360	1632 $\pm$ 143	1432 $\pm$ 152	2001 $\pm$ 182	9.07 $\times 10^{-3}$
10	0	360	1687 $\pm$ 167	1455 $\pm$ 182	2285 $\pm$ 234	9.37 $\times 10^{-3}$
50	0	360	2025 $\pm$ 290	1734 $\pm$ 324	2789 $\pm$ 188	1.13 $\times 10^{-2}$
0	0.33	360	1988 $\pm$ 237	1691 $\pm$ 182	2338 $\pm$ 146	1.10 $\times 10^{-2}$
0	1.67	360	2238 $\pm$ 399	1825 $\pm$ 297	2875 $\pm$ 221	1.24 $\times 10^{-2}$
0	3.33	360	2728 $\pm$ 349	1958 $\pm$ 350	3568 $\pm$ 438	1.52 $\times 10^{-2}$

^aEffluents collected at 1.5, 2, 2.5, and 3 PVs (Figures 2 and 3) were used for r_h measurements.

^bRetentates retained at the column inlet (0–1 cm) were used for r_h measurements.

^c r_h difference of NHs in the effluents and retentates.

^d r_{50} is the average sand grain radius (180 μ m). The r_h/r_{50} values were calculated to test the effect of straining on the retention of CNT-Fe₃O₄ NHs in column experiments.