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Divalent cation contributions to the co-transport and deposition of functionalized multi-walled carbon nanotubes in porous media in the presence of bentonite or goethite nanoparticles: Experiment and simulation

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\textbf{ABSTRACT}

This work investigates the influence of cation type (Ca\textsuperscript{2+} as compared to K\textsuperscript{+}) on the co-transport and deposition of functionalized multi-walled carbon nanotubes (MWCNTs) with negatively (bentonite nanoparticles, BNPs) or positively (goethite nanoparticles, GNPs) charged natural nanoparticles under the same ionic strength (IS = 1 mM) conditions. In packed column tests with quartz sand (QS), the co-transport of MWCNTs was slightly increased by BNPs and inhibited by GNPs in both CaCl\textsubscript{2} and KCl solutions, whereas the co-transport of BNPs or GNPs was facilitated by MWCNTs in both solutions. However, the co-transport of MWCNTs in the presence of BNPs or GNPs exhibited a different dependency on the cation type in quartz crystal microbalance with dissipation (QCM-D) tests. No deposition of MWCNTs and BNPs was observed in QCM-D studies in the presence of KCl, while enhanced deposition of MWCNTs and GNPs occurred in this same solution. In contrast, the deposition of both MWCNTs and BNPs or MWCNTs and GNPs increased in QCM-D in the presence of CaCl\textsubscript{2}. In both column and QCM-D studies, Ca\textsuperscript{2+} exhibited a more significant impact on co-transport than K\textsuperscript{+}, especially for MWCNTs with GNPs than BNPs. Results from molecular dynamic simulations, aggregation studies, and interaction energy calculations indicate that non-DLVO interactions (e.g., H-bonding and cation-n interaction) between two nanoparticles (MWCNTs with BNPs or GNPs) played a non-negligible role in interpreting the deposition and co-transport in the presence of the divalent cation Ca\textsuperscript{2+}. Mathematical modeling of breakthrough curves and retention profiles and aggregation results suggest that both straining and competitive blocking were enhanced and played dominant roles in the co-transport of MWCNTs in the presence of BNPs or GNPs in QS, especially in the presence of Ca\textsuperscript{2+}. This work sheds novel insights on the contribution of divalent cations to interactions between two colloids and their co-transport in porous media. This information is needed to assess the environmental fate and risks of engineered nanoparticles (ENPs) and natural nanoparticles in aquatic and soil environments with abundant divalent cations.

\section{Introduction}

Carbon nanotubes (CNTs), which are allotropes of carbon with a cylindrical-shaped nanostructure (Iijima, 1991), have been employed in numerous commercial applications (Gohardani et al., 2014), including electrical cables and wires (Janas et al., 2014), solar cells (Guldi et al., 2005), radar absorption (Lin et al., 2008), and adsorbents for environmental remediation and water treatment (Camilli et al., 2014; Li et al.,...
media surfaces (Shen et al., 2018). Current studies have investigated the particles, surfactant, organic matter, and contaminants (Tian et al., 2012; Mauter and Elimelech, 2008; Pan and Xing, 2012; Zhang et al., 2012). The non-spheric shape of multi-walled CNTs (MWCNTs) exhibited respectively charged natural nanoparticles (BNPs and GNPs, respectively) of ENPs in the presence of both negatively and positively charged colloids and can influence their transport behavior (Syngouna and Chrysikopoulos, 2013; Syngouna et al., 2017; Yang et al., 2012). Liang et al. (2013) and Zhang et al. (2017a) provided further experimental evidence that the release of soil colloids with ionic strength (IS) reduction and cation exchange can facilitate the transport of silver nanoparticles (ENPs) and natural colloids/nanoparticles is needed to better understand the fate of ENPs in water and soil. Furthermore, most previous studies (Chrysikopoulos et al., 2017; Li et al., 2014) mainly focused on the co-transport of negatively charged clay particles and ENPs under unfavorable conditions for their retention, e.g., in quartz sand under ambient pH values. In this case, competitive blocking of deposition sites has been reported to contribute to the enhanced transport of colloids under co-transport conditions (Cai et al., 2016; He et al., 2018). However, natural water and soil environments possess chemical heterogeneity under ambient pH conditions, which includes both negatively charged colloids, such as clay particles, and positively charged colloids, such as iron oxides. In addition, Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is extensively used to interpret surface interactions between two nanoparticles (e.g., ENPs and natural nanoparticles), and/or porous media, which are used to assess environmental risk and transport behavior of ENPs. However, a few recent studies indicated that ENPs can exhibit different aggregation or transport behaviors from DLVO theory (Liu et al., 2017; Zhang et al., 2020). For example, our previous study on the zeta potential of MWCNTs in the presence of negatively and positively charged natural nanoparticles (BNPs and GNPs, respectively) under monovalent cation concentrations in porous media indicated that non-DLVO interactions between CNTs and BNPs or between CNTs and GNPs played a significant role during their co-transport. The relative importance of cation type on the co-transport, deposition, and surface interactions (e.g., non-DLVO interaction) of ENPs in the presence of natural colloids/nanoparticles is therefore expected although these complexities have not yet been fully resolved.

The main objective of this study is to better understand the roles of negatively (BNPs) and positively (GNPs) charged nanoparticles (4 mg L\(^{-1}\)) on the transport and deposition of functionalized MWCNTs (1 mg L\(^{-1}\)) in the presence of monovalent (IS = 1 mM KCl) and divalent (IS = 1 mM CaCl\(_2\)) cations in porous media. Breakthrough curves and retention profiles for MWCNTs, BNPs, and GNPs were determined in column experiments. Numerical models were employed to simulate their co-transport and competitive blocking behaviors. It should be mentioned that similar co-transport and DLVO calculations of MWCNTs in the presence of BNPs or GNPs at an IS = 1 mM KCl have been previously discussed by (Zhang et al., 2022). While data presented in the current paper exhibit similar trends to our earlier paper, this information is used for a novel purpose to identify the relative contribution of divalent cations. In addition, other aggregation experiments, quartz crystal microbalance with dissipation (QCM-D), batch experiments, and molecular dynamic (MD) simulations were conducted to further investigate the deposition and associations of BNPs-MWCNTs or GNPs-MWCNTs. Results provide valuable insight into the roles of natural nanoparticles in facilitated or inhibited transport and deposition of MWCNTs under divalent cation conditions. This knowledge is essential to help researchers better design their filtration system, optimize the maintenance strategies, and effectively quantify the risk of ENPs while divalent cations are available.

2. Materials and methods

2.1. Materials

Radioactively (\(^{14}\)C) labeled MWCNTs (Bayer Technology Services GmbH, Leverkusen, Germany) with a specific radioactivity of 3.2 MBq mg\(^{-1}\) and a specific density of 1.641 g cm\(^{-3}\) (Pauluhn, 2010) were used in this study. The median diameter and length of functionalized MWCNTs were 10–15 and 200–1000 nm, respectively. The surface of MWCNTs was functionalized (e.g., carboxylic groups) to enhance their stability. BNPs and GNPs were prepared from bentonite and goethite colloids (Sigma-Aldrich Chemie GmbH, Munich, Germany). BNPs had a diameter of 5–200 nm, and GNPs had a diameter of 5–120 nm and a length of 60–800 nm. More information on the synthesis, functionalization, and preparation of MWCNTs, BNPs, and GNPs has been given in previous studies (Kasel et al., 2013; Zhang et al., 2022).

Suspensions of \(^{14}\)C-labeled MWCNTs (1 mg L\(^{-1}\)) with different BNPs (0 and 4 mg L\(^{-1}\)) or GNPs (0 and 4 mg L\(^{-1}\)) concentrations at an IS = 1 mM CaCl\(_2\) (molar concentration 0.33 mM L\(^{-1}\)) or IS = 1 mM KCl (molar concentration 1 mM L\(^{-1}\)) were prepared and ultrasonicated 15 min at 65 W. The input concentrations of MWCNTs, BNPs, and GNPs, as well as the IS = 1 mM CaCl\(_2\) and KCl, were selected based on the preliminary aggregation experiments and high accuracy for measurement (data not shown). All the suspensions of MWCNTs and/or natural nanoparticles (BNPs or GNPs) were ultrasonicated again for an additional 10 min before the experiments. The pH (Mettler Toledo MP230 pH meter) of these suspensions was adjusted to 5.4 by incrementally adding HCl or NaOH.

The zeta potentials and hydrodynamic diameters of the MWCNTs suspensions at different concentrations of BNPs or GNPs (0 and 4 mg L\(^{-1}\)) in IS = 1 mM CaCl\(_2\) were measured using a Zetasizer Nano (Malvern Instruments GmbH, 71,083 Herrenberg, Germany) immediately after suspension preparation. The total interaction energies (\(\Phi\)) between a planar quartz surface and a spherical colloid with similar properties to MWCNTs in the presence of BNPs or GNPs in IS = 1 mM CaCl\(_2\) solution were calculated based on the approach of (Bradford and Torkzaban, 2013). More details are given in Section S1 of the Supporting Information (SI).
2.2. Batch experiments

Batch experiments were conducted under quasi-equilibrium conditions (Zhang et al., 2016) in IS = 1 mM CaCl₂ solution using BNPs or GNPs with MWCNTs (OECD, 2006; Zhang et al., 2022). The adsorption of Ca²⁺ (IS = 0–5 mM) onto MWCNTs (1 mg L⁻¹) in the presence of BNPs or GNPs (4 mg L⁻¹) was also determined in batch studies. The binding energies between MWCNTs (1 mg L⁻¹) and BNPs (4 mg L⁻¹), and between MWCNTs (1 mg L⁻¹) and GNPs (4 mg L⁻¹) in IS = 1 mM CaCl₂ were calculated by molecular dynamics (MD) simulations. More details of batch experiments and MD simulations are provided in sections S2 and S3 of the SI, respectively.

2.3. Deposition and aggregation experiments

The deposition of MWCNTs (1 mg L⁻¹) in the presence and absence of 4 mg L⁻¹ BNPs or GNPs under different cation types (IS = 1 mM CaCl₂ or KCl) was quantified using a QCM-D system (Q-Sense Explorer, Böblin Scientific AB, Sweden) with a crystal sensor (SiO₂, QXS 303). QCM-D is conducted on a plate medium, not a porous medium, which has been used to investigate the situ interactions between nanoparticles and media surfaces (Chen et al., 2016; Liu et al., 2012). The same flow velocity as the column experiments (Darcy velocity ~ 0.7 cm min⁻¹) was used in the QCM-D at room temperature using a peristaltic pump (REGLO Digital ISM 596, ISMATEC, Switzerland) (Jin et al., 2022; Jin et al., 2021). MWCNT and BN, and MWCNT and GNP suspensions were either mixed by ultrasonication or not mixed before injection into the QCM-D to further investigate their mutual interactions during deposition. Note that the mixed system has more contact time between two nanoparticles (MWCNTs with BNPs or GNPs) than the no mixed system.

The aggregation kinetics of MWCNTs (1 mg L⁻¹) in the presence and absence of 4 mg L⁻¹ BNPs or GNPs at IS = 1 mM CaCl₂ or KCl were determined by time-resolved DLS measurements. All suspensions were ultrasonicated before initiating aggregation experiments. Next, 1 mL suspension was then transferred to the DLS cell to monitor changes in the hydrodynamic diameter of MWCNTs with/without BNPs or GNPs every 30 s for 40 min. All the QCM-D and aggregation experiments were replicated and exhibited good reproducibility. A summary of the experimental conditions is provided in Table 1.

The net mass of MWCNTs that was retained due to BNPs or GNPs (r_{C/B}) in QS at IS = 1 mM CaCl₂ or KCl were quantified to evaluate mutual contributions during their co-transport. r_{C/B} was calculated using Eq. (Adamczyk et al., 1994) as:

\[ r_{C/B} = \frac{\Delta r_c}{r_s} \]  

where \(\Delta r_c\) is the difference (between co-transport and the corresponding single-specie transport) in the retained mass of MWCNTs in the presence and absence of BNPs or GNPs. r_s is the injected mass of BNPs or GNPs.

2.5. Numerical modeling

A modified version of the HYDRUS-1D computer code (Simunek et al., 2008) was employed to simulate both the transport and retention of MWCNTs, BNPs, and GNPs in quartz sand. The mass balance equations in the aqueous and solid phases for MWCNTs are given as:

\[ \frac{\partial C_c}{\partial t} = \frac{\partial}{\partial z} \left( D \frac{\partial C_c}{\partial z} \right) - \psi_c k_{sc} C_c + \frac{\partial}{\partial z} \left( D \frac{\partial C_c}{\partial z} \right) \psi_c k_{sc} C_c - \frac{\partial}{\partial z} \psi_c k_{sc} C_c - \frac{\partial}{\partial z} \psi_c k_{sc} C_c \]  

\[ \frac{\partial \rho S_c}{\partial t} = 0 \psi_c k_{sc} C_c - \rho_k k_d S_c \]  

where C_c [N L⁻³, N denotes the number of MWCNTs] is the concentration of MWCNT in the aqueous phase, t is time [T, T denotes time units], D [L² T⁻¹, L denotes units of length] is the hydraulic dispersion coefficient of the column experiment, v [T L⁻¹] is the porewater velocity, z [L] is the distance from the column inlet, \(\theta\) [-] is the volumetric water content, \(\psi_c\) [-] is a dimensionless function to account for time- and depth-dependent retention, \(k_{sc}\) and \(k_{dc}\) [T⁻¹] are the first-order retention coefficient and detachment coefficient, respectively, \(\rho_k\) [M L⁻³, M denotes units of mass] is the sand bulk density, and S_c [N M⁻¹] is the concentration of MWCNT in the solid phase. The first and second terms on the right-hand side of Eq. (Akiwue, 1974) account for the dispersive and advective transport of MWCNTs, respectively. The third and fourth terms in Eq. (Akiwue, 1974) are used to describe retention and release to/from the solid phase, respectively. The value of \(\psi_c\) is given in this work as:

\[ \psi_c = \left( 1 - S_c + \frac{\Gamma_c}{S_c^{\psi_{\Gamma}} - \frac{\partial}{\partial z} \frac{\partial}{\partial z} \left( \frac{\partial}{\partial z} \frac{\partial}{\partial z} \right) \right)^{-\beta} \]
where \( S_N \) is the number of BNP or GNP, \( S_{\text{max}} \) is the maximum solid phase concentration of MWCNTs, \( \Gamma_C \) is the area conversion factor between BNPs and MWCNTs, or between GNPs and MWCNTs, \( d_{50} \) is the median sand grain diameter, and \( \beta \) is an empirical parameter that controls the depth-dependency of the retention rate coefficient. The value of \( \beta \) was set to 0.765 for MWCNTs, BNPs, and GNPs based on our previous study with MWCNTs in quartz sand (Zhang et al., 2016; 2017a). The standard HYDRUS-1D code was modified to consider competitive blocking described by Eq. (Bradford et al., 2017).

Similar to the MWCNT, the mass balance equations in the aqueous and solid phases for the BNPs or GNPs are given in this model as:

### Table 1
Experimental conditions and mass recoveries from effluent for all column experiments.

<table>
<thead>
<tr>
<th>( R_C )</th>
<th>( R_S )</th>
<th>( C_{\text{eq(C)}} )</th>
<th>( C_{\text{eq(B)}} )</th>
<th>( C_{\text{eq(G)}} )</th>
<th>( q )</th>
<th>( d_{50} )</th>
<th>( \text{Por.} )</th>
<th>( M_{e_C} )</th>
<th>( M_{s_C} )</th>
<th>( M_{t_C} )</th>
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<th>( M_{s_S} )</th>
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NA denotes not applicable. \( R_C \) is the retardation factor of MWCNTs, and \( R_S \) is the retardation factor of BNPs or GNPs. \( C_{\text{eq(C)}} \), \( C_{\text{eq(B)}} \), and \( C_{\text{eq(G)}} \) are the input concentrations of MWCNTs, BNPs, and GNPs, respectively. \( q \) is the Darcy velocity. \( \text{Por.} \) is the porosity. \( M_{e_C} \), \( M_{s_C} \), and \( M_{t_C} \) are the effluent percentage, the retained percentage, and the total percentage of MWCNTs recovered from the column experiment, respectively. \( M_{e_S} \), \( M_{s_S} \), and \( M_{t_S} \) are the effluent percentage of BNPs or GNPs recovered from the column experiment. The ionic strength is 1 mM CaCl\(_2\) or KCl. The grain size of the QS is 240 \( \mu \)m.

Fig. 1. Aggregation of MWCNTs (1 mg L\(^{-1}\)) in the presence of BNPs or GNPs (4 mg L\(^{-1}\)) in 1 mM CaCl\(_2\) (a) or KCl (b); QCM-D frequency (\( \Delta f \)) and dissipation (\( \Delta D \)) shift of 3rd overtone as a function of attachment time on silica surface (c-d); QCM-D frequency (\( \Delta f \)) of MWCNTs (1 mg L\(^{-1}\)) in the presence of BNPs or GNPs (4 mg L\(^{-1}\)) in 1 mM CaCl\(_2\) or KCl (c), \( \Delta f \) (d) and \( \Delta D/\Delta f \) (e and f) of MWCNTs (1 mg L\(^{-1}\)) in the presence of BNPs or GNPs (4 mg L\(^{-1}\)) in 1 mM CaCl\(_2\) under mixed (ultrasonication after mixed) and no mixed MWCNTs with BNPs or GNPs suspension (ultrasonicated) before injection into QCM-D.
where the subscript S parameters indicate that they are associated with the BNPs or GNPs. The value of \( \psi_s \) is given as:

\[
\psi_s = \left( \frac{S_i + \Gamma S_e}{S_{net}} \right) \left( \frac{d_0 + \varepsilon}{d_0} \right) \tag{7}
\]

Eqs. (Bradford et al., 2017) and (Bradford et al., 2002) describe the possibility of single species and competitive Langmuirian blocking. Three model formulations for MWCNTs, BNPs, and GNPs retention were considered in this study. The single species transport (model M1) of MWCNTs, BNPs, or GNPs with Langmuirian blocking (Adamczyk et al., 1994) is accounted for using the first term on the right-hand side of these equations when \( \Gamma_c \) and \( \Gamma_s \) are set to zero (including both time- and depth-dependent blocking, \( \beta = 0.765 \)), respectively, whereas competitive blocking (Becker et al., 2015; Zhang et al., 2019) is considered when \( \Gamma_c \) and \( \Gamma_s \) are greater than zero (model M2). The M3 model considers only time-dependent (Langmuirian blocking) retention by setting \( \beta = 0, \) \( \Gamma_c, \) and \( \Gamma_s \) equal to zero. More details of numerical modeling are given in the Section S4 of the SI.

3. Results and Discussion

3.1. Interactions and Aggregation of MWCNTs in the Presence of BNPs or GNPs at IS = 1 mM CaCl₂

The aggregation kinetics of MWCNTs in the presence and absence of BNPs or GNPs at IS = 1 mM CaCl₂ and KCl were performed and are shown in Fig. 1a and 1b, respectively. In the absence of BNPs or GNPs, MWCNTs were not aggregated in both CaCl₂ and KCl solutions due to repulsive forces between negatively charged MWCNTs, indicating that homoaggregation of MWCNTs could be neglected during the transport and deposition of MWCNTs in both CaCl₂ and KCl solutions. In the presence of BNPs or GNPs, the hydrodynamic diameters of MWCNTs-BNPs were stable in KCl solution and showed slight increases in CaCl₂ solution, whereas the hydrodynamic diameters of MWCNTs-GNPs exhibited slight and rapid increases in KCl and CaCl₂ solutions, respectively. Such results demonstrated that divalent Ca²⁺ compared to monovalent K⁺ induced a significantly stronger impact on the interactions between MWCNTs and BNPs, especially between MWCNTs and GNPs. This observation indicated that heteroaggregation could occur during the co-transport and deposition of MWCNTs in the presence of BNPs or GNPs at IS = 1 mM CaCl₂ in this study (Li et al., 2019). Several studies have reported that heteroaggregation quickly occurred between engineered nanoparticles and clay minerals or iron oxides due to cation bridging, electrical interaction, and chemical bonding (Huynh et al., 2012; Labille et al., 2015; Leharte et al., 2015; Sarpong et al., 2017; Wang et al., 2015). The divalent Ca²⁺ compared to monovalent K⁺ could induce heteroaggregation of MWCNTs in the presence of BNPs or GNPs by cation bridging and electrical interaction. Other mechanisms that likely contributed to these observations will be discussed later.

A much higher association was observed between MWCNTs and GNPs than BNPs (Fig. S1). Furthermore, much higher sorption of MWCNTs on BNPs or GNPs occurred in the presence of Ca²⁺ (e.g., nearly complete adsorption) than K⁺ (Zhang et al., 2022). The concave isotherm shape under quasi-equilibrium conditions indicated a low MWCNTs-BNPs or MWCNTs-GNPs affinity at low concentrations. However, adsorption was enhanced with increasing concentration of MWCNTs in the suspension. Our previous studies (Zhang et al., 2022) showed convex, L-shape isotherms of MWCNTs with BNPs or GNPs in 1 mM KCl. In comparison to K⁺, isotherms in the presence of Ca²⁺ show that interactions of MWCNTs with BNPs or GNPs were continuously enhanced, especially for GNPs.

The zeta potentials and hydrodynamic diameters (Table S1) of the MWCNT suspensions in the presence of BNPs or GNPs were measured to better assess the potential effects of MWCNTs-BNPs or MWCNTs-GNPs associations on transport processes. The zeta potentials of mixed MWCNTs-BNPs or MWCNTs-GNPs suspension were more negative in the presence of BNPs and less negative in the presence of GNPs compared to MWCNT suspensions without BNPs or GNPs at IS = 1 mM CaCl₂ (Table S1). The zeta potential of the sand was negative (−25.6 mV, IS = 1 mM CaCl₂). Similar to the electrostatic interaction between MWCNTs and QS, the electrostatic interaction between the MWCNTs-BNPs or MWCNTs-GNPs suspension and QS is still unfavorable. However, the zeta potentials of MWCNTs-BNPs or MWCNTs-GNPs suspension decreased compared to BNPs or GNPs without MWCNTs at IS = 1 mM CaCl₂. Therefore, the electrostatic interaction between MWCNTs-BNPs and QS, and between BNPs and QS is unfavorable, whereas the electrostatic interaction between GNPs and QS is favorable, and between MWCNTs-GNPs and QS is unfavorable. Fig. S2 presents plots of \( \varphi \) as a function of separation distance (h) when a spherical colloid (with properties similar to MWCNTs in the presence or absence of BNPs or GNPs) approaches the surface of QS in CaCl₂ solution at IS = 1 mM. An energy barrier to the primary minimum is present as the colloid approaches the QS as expected based on electrostatics. However, the height of the energy barrier and the depth of the primary minimum is a strong function of the presence of BNPs or GNPs. The presence of BNPs produced a rapid increase in the energy barrier and the primary minimum of MWCNTs on the QS in CaCl₂. The presence of GNPs also enhanced the energy barrier, whereas it decreased the primary minimum of MWCNTs in CaCl₂ (Fig. S2a). Consequently, these observations indicate that positively charged GNPs or negatively charged BNPs might not completely result in “unfavorable” and “favorable” conditions for the attachment of MWCNTs to QS as expected based on only electrostatic considerations. In addition, the presence of MWCNTs enhanced the energy barrier of BNPs or GNPs on the QS in CaCl₂, especially for GNPs (Fig. S2a and S2b). The energy barrier between two nanoparticles (MWCNTs with BNPs or GNPs) in Fig. S2c also suggested that heteroaggregation occurred much easier between MWCNTs and GNPs than between MWCNTs and BNPs. Note that the presence of Ca²⁺ decreased the energy barrier and primary minimum between MWCNTs-BNPs or MWCNTs-GNPs aggregates and QS compared to the monovalent cation of K⁺ (Fig. S2d and S2e).

3.2. QCM-Deposition Kinetics of MWCNTs with BNPs or GNPs in the Presence of Different Cations

QCM-D was used to measure the deposition kinetics during the co-transport of MWCNTs with BNPs or GNPs in IS = 1 mM CaCl₂ or KCl on a silica surface. The QCM-D frequency (Δf) and dissipation (Δθ) shift of the 3rd overtone are shown in Fig. 1 and S3 as a function of attachment time on the silica surface. Both MWCNTs, BNPs, and GNPs were not deposited on the silica surface during single-species transport under IS = 1 mM CaCl₂ or KCl (QCM-D tests, Fig. S3a and b). No deposition of MWCNTs and BNPs was also observed on the silica surface in IS = 1 mM KCl (Fig. 1c), whereas the deposition of MWCNTs and GNPs was enhanced in this same electrolyte solution during their co-transport. The lack of deposition (close to zero) of MWCNTs in the presence of BNPs (IS = 1 mM KCl) was attributed to the large energy barrier (Fig. 1e and S3e). The slightly enhanced deposition (close to −1, Fig. 1c) of MWCNTs and GNPs in IS = 1 mM KCl was potentially due to heteroaggregation of MWCNTs and GNPs, and/or nanoscale heterogeneities (e.g., variations in charge and roughness) on particle surfaces.

The QCM-D deposition of MWCNTs with BNPs or GNPs was enhanced (Fig. 1c) compared to single-species transport of MWCNTs, BNPs, or GNPs in the presence of IS = 1 mM CaCl₂ (compared with 1 mM KCl), with GNPs exhibiting a more significant effect than BNPs on such
deposition. These results suggested that \( \text{Ca}^{2+} \), in comparison to \( \text{K}^{+} \), enhanced the interaction between two nanoparticles (MWCNTs with BNPs or GNPs), and between the two nanoparticles (MWCNTs with BNPs or GNPs) and silica, promoting their deposition. However, the deposition behavior of MWCNTs with BNPs or GNPs in IS = 1 mM CaCl\(_2\) solution also depended on the system mixing (Fig. 1d). The suspension of MWCNTs and BNPs exhibited similar deposition behavior in IS = 1 mM CaCl\(_2\) solution under both mixed and no-mixed conditions, whereas more deposition occurred for MWCNTs and GNPs in the mixed systems (Fig. 1d). This result suggests that \( \text{Ca}^{2+} \) had a continuing effect on the interaction between MWCNTs and GNPs.

The \( \Delta D/\Delta f \) slopes were mainly close to zero in the single-species deposition experiments of MWCNTs, BNPs, and GNPs under IS = 1 mM CaCl\(_2\) (Fig. S3c) or KCl (Fig. S3d), suggesting that a deposited layer was not formed during the single-species transport in the QCM-D. The interaction between GNPs and silica surface might not be strong enough to overcome the mechanical oscillations and shear forces from the flow field of QCM-D, resulting in limited deposition of GNPs under IS = 1 mM CaCl\(_2\) or KCl. In the co-transport of MWCNTs and BNPs, the \( \Delta D/\Delta f \) slopes were still close to zero in IS = 1 mM KCl (Fig. S3e), whereas slow- and fast-slope regions were obtained in IS = 1 mM CaCl\(_2\) (Fig. 1e). The \( \Delta D/\Delta f \) slopes mostly stayed constant in the co-transport of MWCNTs and GNPs in IS = 1 mM CaCl\(_2\) (Fig. 1f) or KCl (Fig. S3f) solutions, suggesting that the viscoelasticity characteristics of the deposited layer did not change during the deposition process (Marcus et al., 2012). The \( \Delta D/\Delta f \) slopes included slow- and fast-slope regions in the
non-mixed suspension with MWCNTs in the presence of BNPs or GNPs at an IS = 1 mM CaCl₂. In this case, the slow-slope region was close to zero in the presence of BNPs (Fig. 1e), while it was slightly greater than zero in the presence of GNPs (Fig. 1f). The deposition layer of two nanoparticles (MWCNTs with BNPs or GNPs) apparently depended on the formation of MWCNTs-BNPs or MWCNTs-GNPs aggregates (Fig. 1e, 1f, and S3e). In addition, the ΔD/Δf slopes of MWCNTs and GNPs are consistently lower than those of MWCNTs and BNPs in both mixed and no-mixed conditions, suggesting that the deposited layer of MWCNTs is relatively harder and denser than that of MWCNTs and BNPs (Gutman et al., 2013; Jin et al., 2022). QCM-D results were consistent with the aggregation and interaction energy between two nanoparticles (MWCNTs with BNPs or GNPs). In brief, divalent Ca²⁺ promoted a continued effect on the formation of MWCNTs-BNPs or MWCNTs-GNPs aggregates compared to monovalent K⁺, especially for MWCNTs-GNPs aggregates, that resulted in their deposition.

### 3.3. Column Co-Transport of MWCNTs with BNPs or GNPs in the presence of different cations

Fig. 2a and b (IS = 1 mM CaCl₂, and 2e and 2f (1 mM KCl) present observed and simulated (M1 model) BTCs and RPs, respectively, for MWCNTs in QS when the input concentrations of BNPs or GNPs were 0 and 4 mg L⁻¹. Fig. 2e and d, and 2g and 2h present corresponding BTCs and RPs for BNPs and GNPs, respectively. The experimental conditions and mass balance information are presented in Table 1. The total mass balance for MWCNTs (M₁), BNPs (M₂), and GNPs (M₃) in the column experiments was very good (>93%, Table 1). Fitted model parameters and their standard error coefficients of M1 and M2 models are given in Tables S2 (dispersion coefficient, kₛ, and kₐc) and S3, along with the Pearson correlation coefficient (R²) and Akaike information criterion (AIC) (Akaike, 1974) for the goodness of fit.

The effect of Ca²⁺. MWCNTs exhibited limited breakthrough and significant retention in the presence and absence of BNPs or GNPs when the IS = 1 mM CaCl₂. BNPs produce a slight increase in the mass percentage recovered in the effluent for MWCNTs (Fig. 2a, e.g., from 0.1% to 0.4% when the BNPs C₀ increased from 0 to 4 mg L⁻¹, respectively), which is shown in Table 1. The asymmetric shape of the BTCs was well described with the M1 model with Langmuirian blocking (R² > 0.99) shown in Eqs. (2)-(4), which attributes the increasing values of Cₑ₀ with suspension injection to blocking or filling of a limited number of retention sites. Retention sites are filled more rapidly for higher retention rates, lower retention capacities, and higher input concentrations (Lei et al., 2015). Note that fitted values of kₛ, kₐc, Sₑ₀/C₀ and Sₙ/C₀ all decreased in the presence of BNPs (Table 1). The decreasing retention rate and capacity with BNPs may be partially explained by greater amounts of electrostatic repulsion. In addition, the presence of BNPs also decreased Sₑ₀/C₀ and thereby enhanced its blocking. If competitive blocking is considered, then retention of BNPs will also contribute to the filling of the MWCNT Sₑ₀ (Becker et al., 2015; Zhang et al., 2019).

Collectively, these results indicate that the presence of BNPs enhanced the transport of MWCNT by (i) altering the solid surface chemistry to create more electrostatically repulsive conditions and (ii) increased blocking and/or competitive blocking. In this work, BTCs of MWCNTs (Fig. 2a) and BNPs (Fig. 2c) were both enhanced during the co-transport in comparison to their individual transport. This mutually facilitated transport of MWCNTs and BNPs in QS suggested that competitive blocking was potentially the dominant mechanism. The M2 model (Fig. S4, Tables 2 and S2) with competitive blocking was therefore used in the further analysis. Values of R² and AIC (Akaike, 1974) also indicate that the M2 model exhibited good simulated results (Fig. S4 and Table 2). Both of Γₑ and Γₛ were >0, suggesting that competitive

### Table 2

<table>
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<tr>
<th>Model</th>
<th>AICc</th>
<th>AICd</th>
<th>Sₑ₀/C₀</th>
<th>Rₑ₀</th>
<th>kₛ</th>
<th>Sₑ₀/C₀</th>
<th>Rₑ₀</th>
<th>kₛ</th>
<th>R²</th>
<th>R²d</th>
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<td>Co (MWCNTs)</td>
<td>1 mg L⁻¹, Co (BNPs/GNPs) = 0 mg L⁻¹, 1 mM CaCl₂</td>
<td>M1</td>
<td>-112.2</td>
<td>2.752</td>
<td>NF</td>
<td>62.91</td>
<td>NF</td>
<td>NF</td>
<td>NF</td>
<td>0.997</td>
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<tr>
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<td>M1</td>
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<td>NF</td>
<td>59.03</td>
<td>30.16</td>
<td>NF</td>
<td>0.999</td>
<td>NF</td>
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<tr>
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<td>M1</td>
<td>-119.3</td>
<td>NF</td>
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<td>45.00</td>
<td>NF</td>
<td>0.998</td>
<td>NF</td>
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<td>2.322</td>
<td>NF</td>
<td>56.32</td>
<td>2.553</td>
<td>NF</td>
<td>0.995</td>
<td>0.988</td>
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<td>NF</td>
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<td>-320.5</td>
<td>2.796</td>
<td>NF</td>
<td>22.76</td>
<td>NF</td>
<td>0.988</td>
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<td>Co (MWCNTs)</td>
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<td>1.354</td>
<td>NF</td>
<td>15.19</td>
<td>1.397</td>
<td>NF</td>
<td>0.910</td>
<td>0.747</td>
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<tr>
<td>Co (MWCNTs)</td>
<td>1 mg L⁻¹, Co (GNPs) = 4 mg L⁻¹, 1 mM KCl</td>
<td>M1</td>
<td>-226.1</td>
<td>1.354</td>
<td>NF</td>
<td>15.19</td>
<td>1.397</td>
<td>NF</td>
<td>0.910</td>
<td>0.747</td>
</tr>
</tbody>
</table>

Sₑ₀/C₀ and kₛ are the normalized maximum solid phase concentration and the first-order retention rate coefficient of MWCNTs, respectively; Sₑ₀/C₀ and kₛ are the normalized maximum solid phase concentration and the first-order retention rate coefficient of BNPs or GNPs, respectively; NF denotes not fitted; R² and R²d are the correlation of observed and fitted data for MWCNTs, and for BNPs or GNPs in the M1 model, respectively. AICc and AICd are the Akaike information criterion for MWCNTs, and for BNPs or GNPs in the M1-M3 models. Fₜ is the area conversion factor between BNPs and MWCNTs, or between GNPs and MWCNTs; Rₑ₀ is the area conversion factor between MWCNT and BNPs, or between MWCNTs and GNPs. The fitted parameters of dispersion coefficient, kₛ, and kₐc are in Table S2.
block the expected to play a role in enhancing MWCNT transport in the presence of BNPs.

The RPs for MWCNTs and BNPs all exhibited hyper-exponential shapes that were well described with the M1 model (Fig. 2b and d) that included a depth-dependent retention function (Eq. 4) with $d = 0.765$. Several factors can contribute to particle retention under electrostatically repulsive conditions and hyper-exponential RPs. The presence of BNPs enhanced the energy barrier and the primary minimum of MWCNTs on the QS, whereas particle interaction in a primary minimum may occur for certain conditions that dramatically reduce and/or eliminate the repulsive energy barrier. For example, the barrier height and adhesive interaction have been reported to be sensitive to the particle shape and orientation (Gomez-Flores et al., 2019; Shen et al., 2016), chemical heterogeneity (Hamamoto et al., 2019; Zhang et al., 2016), and particle shape and orientation (He et al., 2018; Wang et al., 2012). In addition, surface and pore straining processes have been shown to significantly contribute to particle retention under electrostatically unfavorable conditions by altering the lever arms (Treumann et al., 2014; Zhang et al., 2016). A detailed determination of the relative importance of these factors has been addressed in previous works (Zhang et al., 2016; 2017a) but is beyond the scope of the present study.

In contrast to BNPs, GNPs generally exhibit a positive charge in natural aquatic and soil environments. In this work, the zeta potential for GNPs in IS = 1 mM CaCl$_2$ was 27.2 mV (Table S1). Note that most previous co-transport studies have not considered colloids with net positive charges. In contrast to the co-transport of MWCNTs and BNPs, Fig. 2a shows that the transport of MWCNTs was slightly diminished ($M_{\text{max}}$ from 0.1% to 0.03%, Fig. 2a, Table 1) in the presence of 4 mg L$^{-1}$ compared to the absence of GNPs. This resulted in a corresponding slight increase in the solid phase mass percentage (e.g., 98.5% to 100.5%, Table 1, Fig. 2b) for MWCNTs in the presence of GNPs. In contrast to MWCNTs, the breakthrough of GNPs in the effluent slightly increased from 1.2% to 3.5% ($M_{\text{max}}$, Fig. 2c, Table 1) as the input concentration of MWCNTs increased from 0 to 1 mg L$^{-1}$, resulting in a corresponding decrease in the solid phase mass percentage of GNPs from 102.2% to 98.0% ($M_{\text{max}}$, Fig. 2d, Table 1). The BTCs for MWCNTs in the presence of GNPs (Fig. 2a) were well described using the M1 model ($R^2 > 0.99$ in Table 2). Note that fitted values of $k_{\text{C}}$ were very large in the presence of GNPs (Table 2), which delays the breakthrough of MWCNTs until blocking decreases the number of available retention sites. Furthermore, the values of $k_{\text{G}}$ and $S_{\text{max}}/C_0$ for MWCNTs increased due to the presence of GNPs (Table 2). This implies that the rate and capacity for MWCNT retention increased with the GNPs concentration. In addition, some individual GNPs could attach to the QS and apparently created positively charged sites on the sand that were electrostatically favorable for the retention of negatively charged MWCNTs. Furthermore, the GNPs associated with MWCNTs had free positive charges and thus interacted with QS as solid bridges. The association between MWCNTs and GNPs also created a less negatively charged suspension of MWCNTs (Table S1). The BTCs for GNPs (Fig. 2c) were also adequately described using the M1 model ($R^2 > 0.99$ in Table 2). Fitted values of $k_{\text{G}}$ and $S_{\text{max}}/C_0$ for GNPs were high but decreased due to the presence of MWCNTs. The retention of positively charged GNPs on the negatively charged QS surface is electrostatically favorable. However, the observed blocking behavior for GNPs indicates that there was only a limited number of retention sites for GNPs on the QS and that these sites were rapidly filled due to nanoscale roughness that creates shallow primary minimum interactions (Zhang et al., 2022; Zhang et al., 2016). In addition, similar to the co-transport of MWCNTs and BNPs, the M2 model with limited competitive blocking also exhibited a good description for the co-transport of MWCNTs and GNPs (Fig. S4 and Table 2). Both $F_\text{C}$ and $F_\text{G}$ were $0$, suggesting that competitive blocking also plays a role in enhancing MWCNT transport in the presence of GNPs (Zhang et al. 2019; Zhang et al. 2022).

Fig. 2b and d show that the RPs for MWCNTs and GNPs, respectively, were well described using the model that accounted for Langmuirian blocking and depth-dependent (hyper-exponential) retention. This observation suggests that similar retention mechanisms contributed to the retention of both MWCNTs and GNPs, even though those colloids are oppositely charged. In addition to the retention mechanisms for MWCNTs and BNPs (e.g., surface roughness, surface straining processes, and charge heterogeneity) discussed in the previous section, GNPs contribute to retention through favorable electrostatic interactions.

**The effect of cation valence.** Additional experiments were conducted to investigate the effect of cation valence ($Ca^{2+}$ or $K^+$) on the co-transport of MWCNTs (1 mg L$^{-1}$) in the presence of BNPs or GNPs (4 mg L$^{-1}$). Fig. 2e–h present similar information to Fig. 2a–d when the background electrolyte solution was CaCl$_2$ at IS = 1 mM. The enhancement (BNPs) or reduction (GNPs) of MWCNT transport by BNPs or GNPs was more obvious in the presence of IS = 1 mM KCl than CaCl$_2$ (Fig. 2a and e). Similarly, greater transport of BNPs occurred than GNPs, especially in the presence of IS = 1 mM KCl than CaCl$_2$ (Fig. 2e and g). These same trends were reflected in the calculated mass balance values and fitted model parameters. Differences in the interaction of GNPs and BNPs for the MWCNTs and the sand grains were discussed in previous sections. Table 2 indicates that fitted values of $k_{\text{C}}$, $k_{\text{G}}$, $S_{\text{max}}/C_0$, and $S_{\text{max}}/C_0$ (Table 2) were higher in the presence of $Ca^{2+}$ than $K^+$. These observations indicate that $Ca^{2+}$ produced a stronger adhesive force than $K^+$ due to localized neutralization and/or reversal of surface charge (Grosberg et al., 2002; Zhang et al., 2017a), and/or cation bridging (Torkzaban et al., 2012). These same factors can also contribute to greater interactions between two nanoparticles (MWCNTs with BNPs or GNPs) in the presence of $Ca^{2+}$ than $K^+$. These observations indicate that divalent $Ca^{2+}$ cations strongly enhanced competitive blocking in porous media compared to monovalent $K^+$ cations.

The calculated values of $r_{\text{C/G}}$ (mg mg$^{-1}$) reflect the net mass of MWCNTs that were retained due to attached BNPs or GNPs, which are shown in Fig. S6 as a function of BNPs and GNPs concentrations. It was found that values of $r_{\text{C/G}}$ were $\sim 7.5E-03$ and $\sim 8.3E-03$ mg mg$^{-1}$ when the concentration of BNP was 4 mg L$^{-1}$ at IS = 1 mM CaCl$_2$ and KCl, respectively (Fig. S6), but changed to 5.0E-03 and 5.0E-02 mg mg$^{-1}$ when the concentration of GNPs was 4 mg L$^{-1}$. The retardation factors of $F_\text{C}$ and $F_\text{G}$ were significantly greater in the co-transport of MWCNTs with BNPs or GNPs in the presence of $Ca^{2+}$ than $K^+$ (Torkzaban et al., 2012). Note that both $F_\text{C}$ and $F_\text{G}$ were significantly greater in the co-transport of MWCNTs with BNPs or GNPs in the presence of $Ca^{2+}$ than $K^+$, suggesting that divalent $Ca^{2+}$ cations strongly enhanced competitive blocking in porous media compared to monovalent $K^+$ cations.

**3.4. Potential mechanisms.**

The co-transport and deposition of MWCNTs with BNPs or GNPs exhibited different behaviors in column and QCM-D systems. The contribution of $Ca^{2+}$ to retention was significantly greater than $K^+$ when the IS = 1 mM, especially for MWCNTs and GNPs in both column and QCM-D studies. Such phenomena could not be explained just by cation bridging, charge heterogeneity, and heteroaggregation, so other mechanisms likely contributed to these observations.

**Straining and Competitive Blocking.** Deposition trends for MWCNTs in column and QCM-D studies were similar when the IS = 1 mM KCl, while differences were observed in IS = 1 mM CaCl$_2$. Competitive blocking/depocion can occur in column and QCM-D tests, but straining, which is one mechanism of nanoparticle removal in porous media, can only occur in column tests. Column results were simulated with M1 (Langmuirian blocking and depth-dependent retention), M2 (Langmuirian competitive blocking and depth-dependent retention), and M3 (Langmuirian blocking) models to better identify the relative contributions of competitive blocking and straining. The M1 and M2 models (Fig. 2 and...
Table 2 showed a better description than the M3 model (Fig. S5 and Table 2). Depth-dependent retention has been associated with the straining process (Lin et al., 2021), indicating that straining likely played an important role in the co-transport of MWCNTs in the presence of BNPs or GNPs in both IS = 1 mM CaCl₂ and KCl solutions. The cation Ca²⁺ enhanced MWCNTs-BNPs or MWCNTs-GNPs aggregation (Fig. 1a) and thus the deposition of MWCNTs with BNPs or GNPs in QCM-D (Fig. 1c). The ratio of particle diameter to sand grain diameter in the co-transport of MWCNTs with BNPs (0.0032 for MWCNTs-BNPs aggregates) or GNPs (0.0045 for MWCNTs-GNPs aggregates) is much higher than in single-species transport of MWCNTs (0.001). Therefore, hetero-aggregation between two nanoparticles (MWCNTs with BNPs or GNPs) produced larger hydrodynamic diameters (Fig. 1a, Table S1) that should further enhance straining (the ratio of particle diameter to sand grain diameter > 0.0017) processes even under unfavorable conditions (Bradford and Torkzaban, 2015; Bradford et al., 2002; Zhang et al., 2016). Increased straining in the presence of Ca²⁺ is also consistent with more hyper-exponential RPs for both MWCNTs, BNPs, and GNPs (Fig. 2) and higher values of Sₘₐₓ and Sₘₐₓ in the M1, M2, and M3 models (Table 1). Therefore, both straining and competitive blocking were enhanced by Ca²⁺ compared to K⁺ in the co-transport of MWCNTs in QS in column tests, while competitive blocking and zeta potential alteration can only explain the enhanced breakthrough in co-transport experiments in QS (e.g., MWCNT in the presence of BNPs, and GNPs in the presence of MWCNTs). To summarize, different deposition behaviors of two nanoparticles (MWCNTs with BNPs or GNPs) in column and QCM-D systems suggested that both straining and competitive blocking play dominant roles in their co-transport in QS.

**Cation Bridging and Non-DLVO Interaction.** Ca²⁺ produced stronger interactions between two nanoparticles (MWCNTs with BNPs or GNPs) than K⁺, especially for MWCNTs and GNPs, during their co-transport and deposition. Previous studies indicated that divalent Ca²⁺ enhanced the interaction between negatively charged colloids due to cation bridging and alteration of zeta potentials (Shi et al., 2022; Zhu et al., 2022). The adsorption isotherms of Ca²⁺ on MWCNTs, BNPs, and GNPs are shown in Fig. S7. Results indicate that the adsorption capacities of Ca²⁺ followed the order of MWCNTs > BNPs > GNPs. GNPs could still adsorb a very small amount of Ca²⁺, probably due to the free hydroxy groups on the surface of GNPs (Zhang et al., 2022). Therefore, while cation bridging may occur in the association between MWCNTs and GNPs, it plays a more dominant role in MWCNTs and BNPs.

Molecular dynamics (MD) simulations were conducted to investigate the interactions between two nanoparticles (MWCNTs with BNPs or GNPs) in IS = 1 mM CaCl₂ (Fig. 3) and KCl (Zhang et al., 2022). The binding energies of BNPs (Fig. 3a) and GNPs (Fig. 3b) with MWCNTs in IS = 1 mM CaCl₂ were −125.9 ± 7.0 kJ mol⁻¹ and −181.2 ± 7.5 kJ mol⁻¹, which is equivalent to −50.8 and −73.2 kT (1 kT = 2.476 kJ mol⁻¹) (Gupta and Srivastava, 2020) respectively. In addition, MD simulations show that MWCNTs can be completely wrapped by GNPs with a smaller mean distance (0.45 nm, Fig. 3b) between the centroids of MWCNTs. Although MWCNTs were also wrapped by BNPs, much greater dispersion around MWCNTs than GNPs was observed, resulting in a larger mean distance (0.49 nm, Fig. 3a) between the centroids of MWCNTs. The tiny difference of 0.45 and 0.49 nm was in good agreement with the observation of enhanced hydrodynamic...
nanoparticles (MWCNTs with BNPs or GNPs) were observed in IS with divalent Ca cations. Similar to the MD simulation between two nanoparticles (MWCNTs with BNPs or GNPs) in IS with 1 mM KCl (Zhang et al., 2022), the MD simulations in IS with 1 mM CaCl2 also demonstrate that non-DLVO interactions (e.g., H-bonding and cation–π interaction) between two nanoparticles (MWCNTs with GNPs) are thermodynamically feasible (Dougherty, 2013; Patino et al., 2020) and even stronger than in IS with 1 mM KCl, which absolutely contributes to the deposition and interaction behavior of MWCNTs with GNPs during their co-transport. Therefore, Ca2+ could facilitate the non-DLVO interactions between two nanoparticles (MWCNTs with BNPs or GNPs) during IS processes and potentially enhance the associations between MWCNTs-BNPs or MWCNTs-GNPs.

In sum, we found that divalent cations could play a more critical role in mechanisms controlling the co-transport of two colloids than monovalent cations, especially when colloids have opposite surface charges. Previous studies indicated that divalent cations induce interactions between two colloids by cation bridging, charge heterogeneity, and alteration of zeta potentials. However, this study found that divalent cations can also enhance surface interactions between two colloids by non-DLVO forces, especially for colloids with opposite surface charges. Consequently, divalent cations can enhance heteroaggregation, straining, and competitive blocking of two colloids during their co-transport. Such information can be further used to understand and assess the rate of ENPs (e.g., MWCNTs) associated with natural nanoparticles (e.g., BNPs and GNPs) in the soil and groundwater. It is also shown that DLVO theory alone may not be an effective tool to assess the interaction between two colloids or nanoparticles (NPs). This may also partially explain why colloids or NPs can still be retained even under unfavorable conditions.

4. Conclusions

This study investigated the co-transport and deposition of MWCNTs and representative natural nanoparticles (negatively charged BNPs and positively charged GNPs) in packed quartz sand columns and QCM-D systems when the IS = 1 mM CaCl2 or KCl. In QCM-D tests, in the KCl solution, no deposition of MWCNTs or BNPs was observed, while enhanced deposition of MWCNTs and GNPs occurred in their co-transport. However, the deposition of both MWCNTs and natural nanoparticles (BNPs or GNPs) was enhanced in the CaCl2 solution. In column tests, the transport of MWCNTs was slightly enhanced or inhibited due to the presence of BNPs or GNPs, respectively, whereas the transport of BNPs or GNPs was facilitated in the presence of MWCNTs in both CaCl2 and KCl solutions. In addition, Ca2+ (in comparison to K+) exerted a much stronger impact on MWCNTs and GNPs than MWCNTs and BNPs. Our comprehensive results indicate that divalent cations such as Ca2+ compared to monovalent cation K+: (i) enhanced interactions of MWCNTs with both positively charged GNPs and negatively charged BNPs through non-DLVO (e.g., H-bonding and cation–π interaction) and DLVO interactions; (ii) increased the contribution of straining and competition blocking in the co-transport of MWCNTs in the presence of BNPs or GNPs in QS; and (iii) induced different interaction mechanisms between MWCNTs and negatively charged BNPs (e.g., cation bridging) or positively charged GNPs (e.g., heteroaggregation due to both DLVO and non-DLVO interactions). All these results imply that divalent cations play a more complex role than monovalent cations in the co-transport of colloids, and that significant non-DLVO interactions, competitive blocking, and straining should be evaluated to better quantify environmental fate and risk assessment in the water and soil. QCM-D and column tests are also proved to be a powerful tool for the colloid transport and deposition, and interactions between nanoparticles and media surface.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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