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5 **Cotransport of Hydroxyapatite Nanoparticles and Hematite Colloids in**
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8 **Saturated Porous Media: Mechanistic Insights from Mathematical Modeling**
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11 **and Phosphate Oxygen Isotope Fractionation**
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Abbreviations

ADE	Advection-dispersion equation
BET	Brunauer-Emmett-Teller
BTC	Breakthrough curve
CFT	Classical filtration theory
DLS	Dynamic light scattering
DLVO	Derjaguin-Landau-Verwey-Overbeek
EDX	Energy-dispersive X-ray
EM	Electrophoretic mobility
ENP	Engineered nanoparticle
FTIR	Fourier transform infrared
HANP	Hydroxyapatite nanoparticle
IEP	Isoelectric point
IS	Ionic strength
NOM	Natural organic matter
PV	Pore volume
RP	Retention profile
SEM	Scanning electron microscope
SSA	Specific surface area
TEM	Transmission electron microscope
VSMOW	Vienna Standard Mean Ocean Water
XRD	X-ray diffraction
$\delta^{18}\text{O}_\text{P}$	Phosphate oxygen isotope ratio
q	Darcy velocity
ζ -potential	Zeta potential

Abstract

The fate and transport of individual type of engineered nanoparticles (ENPs) in porous media have been studied intensively and the corresponding mechanisms controlling ENPs transport and deposition are well-documented. However, investigations regarding the mobility of ENPs in the concurrent presence of another mobile colloidal phase such as naturally occurring colloids (colloid-mediated transport of ENPs) are largely lacking. Here, we investigated the cotransport and retention of engineered hydroxyapatite nanoparticles (HANPs) with naturally occurring hematite colloids in water-saturated sand columns under environmentally relevant transport conditions, i.e., pH, ionic strength (IS), and flow rate. Particularly, phosphate oxygen isotope fractionation of HANPs during cotransport was explored at various ISs and flow rates to examine the mechanisms controlling the isotope fractionation of HANPs in abiotic transport processes (physical transport).

During cotransport, greater mobility of both HANPs and hematite occurred at higher pHs and flow rates, but at lower ISs. Intriguingly, the mobility of both HANPs and hematite was substantially lower during cotransport than the individual transport of either, attributed primarily to greater homo- and hetero-aggregation when both particles are copresent in the suspension. The shapes of breakthrough curves (BTCs) and retention profiles (RPs) during cotransport for both particles evolved from blocking to ripening with time and from flat to hyperexponential with depth, respectively, in response to decreases in pH and flow rate, and increases in IS. The blocking BTCs and RPs that are flat or hyperexponential can be well-approximated by a one-site kinetic attachment model. Conversely, a ripening model that incorporates attractive particle-particle interaction has to be employed to capture the ripening BTCs that are impacted by particle aggregation during cotransport.

A small phosphate oxygen isotope fractionation ($\leq 2\text{‰}$) occurred among HANPs populations during cotransport responding to IS and flow rate changes. This fractionation is most likely a result of hetero-aggregation between hematite and HANPs that favors light phosphate isotopes (P^{16}O_4). This interpretation is further supported by the increase in isotope fractionation at higher ISs (i.e., greater aggregation). However, the fractionation was progressively erased by decreasing flow rate, ascribed to the reduced mass transfer of HANPs between the influent and effluent. Together our findings suggest that the cotransport and retention of HANPs and hematite colloids are highly sensitive to the considered physicochemical factors, and isotope tracing could serve as a promising tool to identify the sources and transport of phosphate-based NPs in complex subsurface environments due to insignificant transport-related isotope fractionation.

Keywords: Hydroxyapatite nanoparticles; Hematite colloids; Porous media; Cotransport; Mathematical modeling; Phosphate oxygen isotope fractionation

1. Introduction

The past decade has witnessed the rapid development of nanotechnology (Roco and Bainbridge, 2013), which is aimed at using materials with specific and novel properties and functions in the length scale of 1–100 nm (National Nanotechnology Initiative, NNI). Nowadays, there are >3000 nanotechnology-based consumer products in the market worldwide (Nanowerk Nanomaterial Database). Being one of the most important inorganic nanoparticles (NPs), hydroxyapatite NPs (HANPs, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) have been employed in the medical fields such as bone tissue engineering applications, intracellular drug delivery, and gene delivery because of

their excellent biocompatibility and bioactivity (Balasundaram et al., 2006; Chen et al., 2011; Zhu et al., 2004). Furthermore, attributable to their nanoscale dimensions, large specific surface area (SSA), and high reactivity, HANPs have been extensively used as an effective absorbent to sequester metals and radionuclides in contaminated soils, sediments, and groundwater, *in-situ* or *ex-situ* (Chen et al., 2010; Handley-Sidhu et al., 2012; Zhang et al., 2010). Recently, HANPs have been advocated as a promising phosphorus (P) nanofertilizer (Liu and Lai, 2014; Montalvo et al., 2015; Wang et al., 2015a). For example, through a greenhouse pot experiment, Liu and Lal (2014) found that application of HANPs enhanced the growth rate and seed yield of soybean (*Glycine max*) by 33% and 20%, respectively, compared to those fertilized by a regular solid P fertilizer ($\text{Ca}(\text{H}_2\text{PO}_4)_2$). This is likely due to HANPs' higher mobility than their bulk counterparts and/or larger reactive surface area allowing greater dissolution and release of P, thereby reaching the rhizosphere and subsequently nurturing crops in a timely fashion. Increasing use of HANPs for medical, environmental, and agronomic advantages will likely result in an unknown spread of HANPs and released P in the subsurface environments.

A more complete understanding of the fate and transport of HANPs in the subsurface environments will guide the selection of the best-suited strategy for *in-situ* remediation of contaminated sites, and optimization of nanofertilizer applications in agricultural soils. Generally, the transport and deposition of NPs in saturated porous media are influenced by the interplay of physicochemical properties of particle and collector surfaces, and solution chemistry and hydrodynamics of the system (e.g., Elimelech et al., 1995; Grolmund et al., 1998; Harter et al., 2000; Petosa et al., 2010; Schijven and Hassanizadeh, 2000; Wang et al., 2015b). Such factors as pH, ionic strength (IS), and flow rate have been documented to have significant impacts on the transport behavior of NPs (Chen et al., 2012; Chowdhury et al., 2011; Jiang et al., 2012; Li et al.,

2008; Wang et al., 2014a; 2015b). Nevertheless, an overwhelming majority of the existing studies are limited to the transport of a single type of NPs in porous media. Few studies have attempted to quantify the mobility of NPs in the copresence of another mobile colloidal phase such as naturally occurring colloids, which have long been recognized as an important vector for transport of both nutrients (Sims et al., 1998) and contaminants (e.g., metals, radionuclides, and organic pollutants) in the subsurface (Cheng and Saiers, 2015; McCarthy and Zachara, 1989; Shen et al., 2015). Iron oxides such as ferrihydrite, goethite, and hematite occur ubiquitously in the subsurface (White and Brantley, 1995), and their mobile colloidal phase is known to play critical roles in the fate, transport, bioavailability, and biogeochemical cycling of P including HANPs due to their high sorption capacity toward P (Frossard et al., 1995; Stumm and Sulzberger, 1991; van der Zee et al., 2003; Waychunas et al., 2005). It is therefore anticipated that the mobility of HANPs in the subsurface is, in part, controlled by the presence of mobile iron oxide colloids. Particularly, we recently demonstrated that transport and retention of HANPs were largely influenced by mobile goethite NPs in response to variability in pH, and type and concentration of natural organic matter (NOM) in saturated porous media (Wang et al., 2015a). However, the effects of other environmentally significant conditions, particularly ionic strength and flow rate on the cotransport of HANPs and naturally occurring iron oxide colloids are nonexistent.

The last decade has also witnessed the burgeoning application of stable oxygen isotope technique in tracing the sources and identifying the biogeochemical cycling of phosphate in natural environments (Blake et al., 1997; Jaisi and Blake, 2014; Joshi et al., 2015; Paytan et al., 2002). This is because orthophosphate (PO_4^{3-}) is cycled primarily via biologically-mediated reactions and the presence of enzymes causes changes in isotopic composition (Blake et al., 1997;

93 Liang and Blake, 2006, 2009; Paytan et al., 2002; Stout et al., 2014). Interestingly, in abiotic
 94 systems, oxygen isotope exchange is insignificant between phosphate and ambient water at low
 95 temperature (<80 °C) and near-neutral pH conditions (Jaisi et al., 2010; Lecuyer et al., 1999; Li
 96 and Jaisi, 2015). More extensive application of oxygen isotope ratios in phosphate ($\delta^{18}\text{O}_\text{P}$) as a
 97 biogeochemical tracer of P sources and cycles, however, relies on a more complete
 98 understanding of all processes and reactions that could (or not) lead to changes of isotopic
 99 compositions as well as fractionation factors for particular reactions or processes. To date, there
 100 is just one study aimed at elucidating the isotope effects during phosphate transport in the
 101 subsurface environments (Jaisi, 2013), thus limits our ability to better predict the variability of
 102 $\delta^{18}\text{O}_\text{P}$ values between subsurface soils and pore-water. Jaisi (2013) found that oxygen isotope
 103 exchange of dissolved phosphate ion between the effluent and influent was ~1.3‰ with
 104 isotopically-lighter phosphate (P^{16}O_4) preferentially retained in the column in the early stage of
 105 transport, and this isotopic fractionation became negligible as more phosphate passed through the
 106 column due to the efficient exchange between aqueous and sorbed phosphate ions over time.
 107 However, the physical and thermodynamic properties of NPs are different from ions, and the
 108 extent of isotope effects of NPs during transport is therefore expected to be different from those
 109 of ions (Steeffel and Van Cappellen, 1990). To accurately trace the sources and identify the
 110 biogeochemical processes of HANPs in the subsurface environments, it is critical to elucidate the
 111 isotope effects of HANPs during transport.

112 The goal of this research was to develop a better understanding of the fate, transport, and
 113 isotope fractionation of HANPs in the copresence of naturally occurring iron oxide (hematite)
 114 colloids in saturated porous media. Our specific objectives were to (i) determine the mechanisms
 115 controlling cotransport and retention of HANPs and hematite colloids under environmentally

relevant transport conditions, i.e., pH, IS, and flow rate; and (ii) elucidate the roles of IS and flow rate on phosphate oxygen isotope fractionation among HANPs populations during cotransport.

2. Materials and Methods

2.1. HANPs and hematite colloids

HANPs (purity >99.9%) were purchased from Nanjing Emperor Nanomaterial Co. Ltd., China. The physicochemical properties of the HANPs have been well-characterized previously (Wang et al., 2012a; 2015a). Briefly, the HANPs are single-phased pure hydroxyapatite mineral and display a rod morphology with mean dimensions of 20 nm wide and 100 nm long. The Ca/P molar ratio and SSA of HANPs are 1.65 and 154 m² g⁻¹ (N₂-BET method), respectively. The hematite colloids were synthesized following the method of Schwertmann and Cornell (2000). Shortly, 300 mL of 1 M KOH was added to 500 mL of 0.2 M Fe(NO₃)₃ while stirring. Fifty mL of 1 M NaHCO₃ was then added to the mixture and the resulting suspension was held in a closed glass flask at 90 °C for 48 h. The synthesized hematite colloids were separated from residual reagents through a DI water wash-centrifugation procedure, freeze-dried, ground with mortar and pestle, and passed through a No. 70 standard sieve (0.212 mm opening) for later use.

The physicochemical properties of the hematite colloids were characterized in this study. Briefly, mineral phase and functional groups of the hematite were identified using X-ray diffraction (XRD; Bruker D8 Advance, Bruker Corp., Billerica, MA) and a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer (Thermo Scientific, Waltham, MA), respectively. The surface morphological features were observed with a scanning electron microscope (SEM; Zeiss

Auriga 60, Carl Zeiss Microscopy GmbH, Jena, Germany). Crystal size and shape of the hematite were examined via a transmission electron microscope (TEM; JEM-3100, JEOL, Japan), and the sample was prepared by placing 2–3 dropsof the hematite stock suspension (see below) on a 100 mesh carbon film-covered copper grid. The SSA was measured through a surface area and porosity analyzer (Micromeritics 3000, Micromeritics Instrument Corp., Norcross, GA) using the BET method. Isoelectric point (IEP) of the hematite suspended in 0.01 M KNO₃ was determined using the Zetasizer Nano ZS (Malvern Instruments, Southborough, MA).

2.2. Preparation of HANPs-hematite influent suspensions

We first prepared a hematite stock suspension. Specifically, 0.050 g of hematite dry powder was added in 500 mL deionized (DI) water. The suspension was sonicated in a water bath at 25 °C for 1 h to disperse particles and was then centrifuged at 350g for 1 min to allow settlement of large aggregated particles (>2 µm diameter)based on the Stokes' law of settling. The supernatant of the suspension was carefully decanted and stored as the hematite stock suspension, and its concentration was measured using aDU Series 640 UV-vis spectrometer (Beckman Instruments Inc., Fullerton, CA) at the wavelength of 460 nm and was ~70 mg L⁻¹ (see supplementary material S1 and Fig. S1).

The HANPs-hematite influent suspension was prepared by weighting 0.030 g of HANPs dry powder to a precalculated volume of the hematite stock suspension, and then diluting the suspension with KNO₃ solution (background electrolyte) to a final volume of 150 mL. The concentrations of HANPs, hematite, and KNO₃ in the influent were 200 mg L⁻¹, 50 mg L⁻¹, and 0.1 mM, respectively. A high concentration of 200 mg L⁻¹ was chosen for HANPs to obtainsufficient amount of phosphate for isotopic measurements (described below). To reveal the

role of pH on the cotransport of HANPs and hematite, the pH of HANPs-hematite influents (background electrolyte of 0.1 mM KNO₃) was adjusted to environmentally relevant values (6.5, 7.5, and 10.5) using 1 mM HNO₃ or NaOH. A pH of 10.5 was chosen to reverse the surface charge of hematite due to its high IEP (pH = 7.0–9.3) (Kosmulski, 2011). Similarly, additional HANPs-hematite influents were prepared with KNO₃ solution and Suwannee River humic acid (SRHA) stock solution (see supplementary material S2) to study the coupled effect of environmentally relevant concentrations of monovalent electrolyte (0.1, 10, and 50 mM KNO₃) (Sigg and Stumm, 2011) and NOM (1 mg L⁻¹ SRHA) (Aiken, 2014) on the cotransport of HANPs and hematite. Solution chemistries of the HANPs-hematite influents are summarized in Table 1.

Electrophoretic mobility (EM) of the HANPs-hematite influents and individual HANPs suspensions at the desired solution chemistries was measured using the Zetasizer Nano ZS, as described earlier (Wang et al., 2012a; 2015a), and converted to zeta (ζ) potentials using the Smoluchowski equation (Elimelech et al., 1995). The average hydrodynamic diameter (D_H) of the HANPs-hematite influents and individual HANP suspensions under different experimental conditions was analyzed using the dynamic light scattering (DLS; Möbius, Wyatt Technology Corp., Santa Barbara, CA). Standard deviations were estimated based on >10 measurements conducted on three replicate samples for each experimental condition. The ζ -potential and D_H value of individual HANPs were then used in combination with the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) to compute the interaction energy between HANPs and sand grains over the range of solution chemistries investigated (see supplementary material S3). TEM was applied to visually examine

the interactions such as homo-aggregation of HANPs and hematite, and hetero-aggregation between HANPs and hematite at selected solution chemistries.

2.3. Column experiments

Quartz sand (Accusand C-190, Unimin Corp., Le Sueur, MN) served as model porous media in the column experiments. The manufacturer reported that the sand is spherical in shape with a medium grain size (d_{50}) of 688 μm . Prior to use, the sand was cleaned thoroughly using a procedure described previously (Wang et al., 2012a; 2015a). The particles from pulverized quartz sand were used as surrogates for the sand and for ζ -potential measurements, as described above.

Three sets of column experiments were conducted to investigate the effects of physicochemical factors on the cotransport and retention of HANPs and hematite in saturated sand columns (Table 1). The first set investigated the role of pH (6.5, 7.5, and 10.5) at IS = 0.1 mM KNO_3 and Darcy velocity (q) = 0.44 cm min^{-1} . The second set studied the impact of IS (0.1, 10, and 50 mM KNO_3) at pH $\sim$ 7.5 and q = 0.44 cm min^{-1} in the presence of 1 mg L^{-1} SRHA, and the last set explored the influence of flow rate (q = 0.44, 0.22, and 0.044 cm min^{-1}) at pH = 7.5 and IS = 0.1 mM KNO_3 . The experimental pH, IS, flow rate, and NOM concentration are chosen to be environmentally relevant with the exception of q = 0.44 cm min^{-1} . The high velocity of 0.44 cm min^{-1} is similar to the typical fluid velocities in coarse aquifer sediments (Harter et al., 2000) or forced-gradient in engineered systems such as in pump-and-treat (Duba et al., 1996) and *in-situ* groundwater remediation technique (Su et al., 2012).

Glass chromatography column (1.7-cm inner diameter and 9-cm long) was used in the column transport studies. The column was dry packed with 31.4 g of the cleaned sand (bulk

density of 1.54 g cm^{-3}) and then purged with CO_2 in an upward flow direction for 30 min to ensure water saturation. Afterwards, DI water was injected in the upward flow direction at $q = 0.044 \text{ cm min}^{-1}$ to slowly saturate the packed column. Column porosity was determined gravimetrically to be ~ 0.30 .

After saturating the column, a nonreactive tracer experiment (50 mM KNO_3) was performed to obtain hydrodynamic parameters for the column by fitting the measured tracer breakthrough curve (BTC) to the one-dimensional advection-dispersion equation (ADE) using the STANMOD code (Simunek et al., 1999). The same injection velocity was chosen in tracer and HANPs-hematite cotransport experiments for a given column. After the tracer test, >20 pore volumes (PVs) of background electrolyte solution were injected in the column to equilibrate pore-water solution chemistry. Five PVs of the HANPs-hematite influent suspension under different experimental conditions (Table 1) were injected in the column, followed by elution with 5 PVs of particle-free background electrolyte solution. The electrolyte concentration and Darcy velocity remained constant during each experiment. During pulse injection, the HANPs-hematite influent was periodically sonicated to avoid particle settlement particularly at low pH and flow rate (Wang et al., 2015a). Column effluents (3.4 mL each) were sampled continuously using the Foxy Jr. fraction collector (Teledyne Isco, Lincoln, NE).

At the conclusion of each cotransport experiment, the column was carefully dissected into 10 layers of 1-cm segments. Retained HANPs and hematite (hereafter referred to as retentate) were released from the sand grains by placing them in DI water or 1 mM NaOH solution (depending on suspension pH), shaking at 50 rpm for 1 h , and sonicating at a low frequency of 20 kHz for 30 min in a water bath at 25°C (Wang et al., 2015a). The concentrations of phosphate in the effluents and retentates were obtained using the phosphomolybdate method

(Murphy and Riley, 1962), which was then used to calculate the concentrations of HANPs in the effluents and retentates. The UV-vis spectrophotometer was employed to quantify hematite concentrations in the effluents and retentates at the wavelength of 460 nm, as described above. Mass balance of HANPs (or hematite) was calculated based on the mass of HANPs (or hematite) in the effluent, the mass in the retentate, and total mass injected in the column.

To reveal the cotransport mechanisms of HANPs and hematite in saturated sand columns, additional experiments were conducted. Dissolution of HANPs at varying pHs was monitored over the time frame of the cotransport experiment in batch experiments, given that HANPs are likely to dissolve at acidic pH (Wang et al., 2015a). Moreover, the D_H of HANPs-hematite samples in the effluents and retentates was measured to assess the aggregation of both particles during cotransport. Additionally, SEM equipped with energy-dispersive X-ray (EDX) spectrometry was used to explore the retention mechanisms of HANPs-hematite on the sand grains at selected solution chemistries.

2.4. Measurements of phosphate oxygen isotope ratios ($\delta^{18}O_P$)

In selected column experiments run at varying ISs and flow rates, HANPs-hematite samples in the influents, effluents, and retentates were individually processed for O-isotopic measurements. All samples were purified using the dissolution and crystallization method (Jaisi and Blake, 2014; Kolodny et al., 1983). We first used 2 M HNO_3 to completely dissolve the HANPs-hematite samples at 60 °C. It was followed by cation resin treatment (Bio-Rad AG50W-X8, Hercules, CA) to remove cations, primarily the Ca^{2+} and Fe^{3+} , in the dissolved solution. For the samples containing SRHA (i.e., at varying ISs), the dissolved solution was first treated by the Supelite™ DAX-8 resin (Sigma-Aldrich) to remove SRHA before removing the cations. Two

separate phosphate standards (10 and 20 $\mu\text{moles Na}_2\text{HPO}_4$) were processed in parallel to test the validity of sample processing and reliability of isotope results. The purified phosphate solution was finally precipitated as silver phosphate (Ag_3PO_4).

All phosphate oxygen isotope ratios ($\delta^{18}\text{O}_\text{P}$) were measured at the stable isotope facility at the University of Delaware. The Ag_3PO_4 was measured by online high-temperature thermal decomposition method using a Thermo-Chemolysis Elemental Analyzer (TC/EA at 1460 $^\circ\text{C}$) coupled to a Delta V continuous flow isotope ratio monitoring mass spectrometer (IRMS; Thermo, Bremen, Germany). The $\delta^{18}\text{O}_\text{P}$ value of each sample was calibrated against two Ag_3PO_4 standards, YR-1aR-02 (-5.49%) and YR-3.2 ($+33.63\%$) (Vennemann et al., 2002). All $\delta^{18}\text{O}_\text{P}$ values in this communication are reported relative to the Vienna Standard Mean Ocean Water (VSMOW) standard in units of permil ($\%$).

2.5. Mathematical modeling

A one-dimensional form of the ADE with one kinetic attachment site was used to simulate the blocking (a decreasing rate of attachment with time) BTCs (Simunek et al., 2013):

$$\frac{\partial(\theta_w C)}{\partial t} = \frac{\partial}{\partial z} \left(\theta_w D \frac{\partial C}{\partial z} \right) - \frac{\partial(qC)}{\partial z} - \theta_w \psi k_a C \quad [1]$$

$$\frac{\partial(\rho_b S)}{\partial t} = \theta_w \psi k_a C \quad [2]$$

where θ_w is the volumetric water content $[-]$, C is the HANPs (or hematite) concentration in the aqueous phase $[\text{M L}^{-3}]$, M and L denote units of mass and length, respectively], t is the time $[\text{T}]$, T denotes time unit], z is the distance from column inlet $[\text{L}]$, D is the hydrodynamic dispersion coefficient $[\text{L}^2 \text{T}^{-1}]$, q is the Darcy velocity $[\text{L T}^{-1}]$, ψ is a dimensionless function to account for both time- and depth-dependent blocking $[-]$, k_a is the attachment rate coefficient of HANPs (or

hematite) from the aqueous phase to solid phase, ρ_b is the bulk density of porous medium [M L⁻³], and S is the solid-phase concentration of retained HANPs (or hematite) [M M⁻¹]. The expression for the blocking term (ψ) is given as follows:

$$\psi = \left(1 - \frac{S}{S_{\max}}\right) \left(\frac{d_{50} + z}{d_{50}}\right)^{-\beta} \quad [3]$$

where d_{50} is the median grain size of porous medium [L], β is an empirical parameter controlling the shape of spatial distribution of retained HANPs (or hematite) [-], and $S_{\max}$ is the maximum solid-phase concentration of retained HANPs (or hematite) [M M⁻¹]. The first term on the right hand side of Eq. [3] accounts for filling of retention sites in a manner similar to the Langmuirian blocking effect (Adamczyk et al., 1994), whereas the second term describes depth-dependent retention, e.g., a decreasing rate of attachment with depth.

While the above model formulation is flexible and can account for blocking BTCs and retention profiles (RPs) that are exponential, uniform, and hyperexponential with depth, consideration of only these factors cannot account for the ripening BTCs (an appreciable increase in deposition with time). Reversible, depth-dependent deposition that includes a term for ripening was therefore used to fit the ripening BTCs as follows:

$$\frac{\partial(\rho_b S)}{\partial t} = \theta_w \psi k_d C - \rho_b k_r S \rho_b + S \theta_w C k_{\text{int}} \quad [4]$$

where k_d is the particle deposition rate coefficient [T⁻¹], k_r is the particle release rate coefficient [T⁻¹], and k_{int} is the particle interaction (e.g., homo- and hetero-aggregation) rate coefficient [L³ T⁻¹ N⁻¹]. Ripening often occurs when attractive particle-particle interaction enhances particle deposition on the collector surface. Enhanced particle-particle deposition due to ripening is simulated using the third term on the right hand side of Eq. [4], which assumes that ripening is second-order with respect to concentration, and thus proportional to the frequency of collisions

between particles in the aqueous phase ($\theta_w C$) and particles immobilized on the collector surface ($\rho_b S$). Please note that reverse the sign of k_{int} can be used to indicate liberation (release) of retained particles when the particle-particle interaction is repulsive.

The one-site kinetic attachment model and the ripening model described above were numerically solved using the HYDRUS-1D code (Simunek et al., 2013). A nonlinear least square optimization routine based upon the Levenberg-Marquardt algorithm (Marquardt, 1963) was incorporated in the HYDRUS-1D code to obtain HANPs and hematite transport parameters, i.e., S_{max} , k_a , and β for the one-site kinetic attachment model, and k_d , k_r , and k_{int} for the ripening model.

2.6. Statistical analysis

To determine the statistical differences among measured parameters in this study, one-way ANOVA analysis was performed using the Tukey's Honestly Significant Different (HSD) test. All analyses were performed in SPSS 16.0 software and the differences of mean values were considered to be significant at the level of $p < 0.05$.

3. Results and Discussion

3.1. Characterization of hematite colloids

Crystallinity and purity of as-synthesized hematite were examined using powder XRD measurement (Fig. 1a). The narrow sharp peaks imply a highly crystalline hematite (PDF 01-076-9683). No other peaks were observed, suggesting the high purity of the hematite. Further evidence for the formation of hematite can be obtained from its FTIR spectrum (Fig. 1b): two strong peaks at 802 and 891 cm^{-1} are the characteristic vibrations of Fe-O bonds (Schwertmann and Cornell, 2000). SEM and TEM images show that the hematite has a spindle morphology with

an average diameter of ~350 nm (Fig. 1c, d). BET measurement indicates that the SSA of hematite is $41.2 \text{ m}^2 \text{ g}^{-1}$, which is in close agreement with literature results (Schwertmann and Cornell, 2000). The IEP of hematite is measured at pH around 9.0, as shown in the supplementary material Fig. S2. This result is consistent with reported IEP values (pH = 7.0–9.3) for hematite (Kosmulski, 2011).

3.2. Electrokinetic properties of HANPs-hematite influents, quartz sands, and individual HANPs suspensions

The ζ -potentials of HANPs-hematite influents, quartz sands, and individual HANPs suspensions at the desired solution chemistries are shown in Table 2. The results indicate that the HANPs-hematite influent, quartz sand, and individual HANPs were negatively charged over the range of solution chemistries studied with the exception of the HANPs-hematite influent at pH 6.5, which is likely because the positively charged hematite (supplementary material Fig. S2) dominates the overall surface charge of the HANPs-hematite complex. The magnitude of ζ -potential for HANPs-hematite influent, quartz sand, and individual HANPs increased with increasing pH, attributed primarily to the dissociation of proton groups on HANPs (Wang et al., 2012b; 2015a), hematite (Hes and Tombacz, 2006), and quartz sand (Stumm and Morgan, 1996), which is a common observation documented in the literature (Elimelech et al., 1995). In the presence of 1 mg L^{-1} SRHA, their ζ -potentials became significantly ($p < 0.05$, Table 2) less negatively charged at higher ISs due to greater compression (charge screening) of electrostatic double layer of particles (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). These results are consistent with previous findings (Elimelech et al., 1995). Regardless of solution chemistry, the magnitude of ζ -potential for the HANPs-hematite influent was always smaller than

that of individual HANPs, due to the presence of positively charged hematite (or less negatively charged hematite relative to HANPs, supplementary material Fig. S2) in HANPs-hematite influent.

3.3. Average hydrodynamic diameters of HANPs-hematite influents and individual HANPs suspensions

The average hydrodynamic diameter (D_H) of NPs is often considered as an indicator of NPs mobility in porous media (Keller et al., 2010; Wang et al., 2014b; 2015a). The D_H values of HANPs-hematite influents and individual HANPs at varying solution chemistries are summarized in Table 3. Apparently, the D_H value of HANPs-hematite influent increased significantly ($p < 0.05$) with decreasing pH, particularly when the pH (6.5 and 7.5) was below the IEP of hematite ($IEP_{\text{hematite}} = 9.0$). This is mainly due to greater homo-aggregation of HANPs and hematite, and hetero-aggregation between negatively charged HANPs and positively charged hematite at lower pH, as expected from their ζ -potentials (Table 2). TEM images of the HANPs-hematite influent at pH 7.5 are shown in Fig. 2, which indicates that both homo-aggregation and hetero-aggregation occurred in the HANPs-hematite influent. Especially, the TEM size of the HANPs-hematite complexes reached up to $\sim 1 \mu\text{m}$ (Fig. 2A). Similar findings were recently reported for the hetero-aggregation between NPs (e.g., carbon nanotube and hematite NPs, and gold and carbon nanotube NPs) (Huynh et al., 2012; Nabiul Afrooz et al., 2013) and between NP and colloid (e.g., TiO_2 NP and SiO_2 colloid, and graphene oxide NP and goethite colloid) (Praetorius et al., 2014; Zhao et al., 2015). However, the D_H value of HANPs-hematite influent increased with increasing IS even in the presence of 1 mg L^{-1} SRHA, suggesting that the SRHA can only stabilize the HANPs-hematite influent to a limited extent. Similar results were obtained

for the homo-aggregation of SRHA-coated hematite colloid with elevating NaCl concentration (Mylon et al., 2004). Again, the D_H value of HANPs-hematite influent was larger than that of individual HANPs at a given solution chemistry, consistent with their ζ -potential trends (Table 2).

Given that the DLVO theory is not applicable to quantify interaction energy between complex (i.e., HANPs-hematite complex) and sand grain, the individual HANP was employed to represent the HANPs-hematite complex for DLVO interaction energy calculation. This is primarily because two critical parameters that determine DLVO interaction energy, i.e., ζ -potential and particle size were comparable over the range of solution chemistries investigated (Tables 2–3). We anticipate that the overall trends of DLVO interaction energy for HANPs-sand system and HANPs-hematite-sand system are similar in response to variability in solution chemistry (see supplementary material S3 in detail).

3.4. Cotransport of HANPs and hematite

3.4.1. Effect of pH

Fig. 3 presents observed and fitted BTCs and RPs of HANPs and hematite, respectively, at varying pHs (6.5, 7.5, and 10.5) when $IS = 0.1 \text{ mM KNO}_3$ and $q = 0.44 \text{ cm min}^{-1}$. The BTCs are plotted as normalized effluent concentrations (C_i/C_o) vs. PVs, and the RPs are plotted as normalized solid-phase concentration (S/C_o) vs. distance from the column inlet. The total mass balances for both HANPs (83.1–109%) and hematite (97.8–111%, Table 1) were good, indicating that our experimental procedures and protocols are reliable. The model-fitted parameters and Pearson's correlation coefficient (R^2) between observed and fitted data are summarized in Table 4, which reflects that either the one-site kinetic attachment model or the

ripening model was able to sufficiently capture the main features of HANPs and hematite cotransport and retention ($R^2 = 0.858-1.00$).

The pH was found to have a significant influence on the cotransport and retention of HANPs and hematite. The greatest mobility of both HANPs and hematite occurred at pH of 10.5 (Fig. 3 and Table 1) due, in part, to the highest electrostatic repulsion between HANPs (including hematite and HANPs-hematite complex) and sand grains (see supplementary material Fig. S3a). In particular, the values of maximum retention capacity ($S_{\max}/C_o$) for both HANPs and hematite obtained at pH 10.5 using the one-site kinetic attachment model (Table 4) were low, meaning that the overall retention for both particles is limited. In addition, the homo-aggregation of HANPs and hematite in the influent was less pronounced at pH 10.5 than at pHs 6.5 and 7.5 (Table 3), further contributing to the high mobility of HANPs and hematite at pH 10.5.

At low pHs of 6.5 and 7.5, both homo-aggregation and hetero-aggregation of HANPs and hematite in the influents were significant (Table 3), thereby yielding the low mobility of both particles (Fig. 3 and Table 1). Specifically, the ripening BTCs were encountered for both particles with the exception of HANPs at pH 6.5 (Fig. 3a, c), signifying that particle (homo- and hetero-) aggregation occurs during cotransport. These observed ripening BTCs can also be quantified by the model-fitted parameters k_{int} , k_d , and k_r , which reflect the interaction between particles (k_{int}), deposition of particles on the solid phase (k_d), and release of particles from the solid phase, respectively (Table 4). The values of k_{int} and k_d were nearly 2-orders of magnitude greater than those of k_r , indicative of the predominance of particle interaction (homo- and hetero-aggregation) and deposition in determining the mobility of HANPs and hematite. Based on the classical filtration theory (CFT) (Yao et al., 1971), deposition mechanisms of interception and sedimentation are expected to play pivotal roles in particle retention since the D_H values of

HANPs-hematite influents at pHs 6.5 and 7.5 were up to 1 μm (Table 3). The SEM-EDX analysis of the particles retained on the sand grains excavated from the column inlet (0–1 cm) after completion of the cotransport test at pH 7.5 supports this hypothesis (Fig. 4).

Surprisingly, the transport of HANPs was approximately 7-fold greater at pH 6.5 than at pH 7.5 ($M_{\text{eff}} = 38.9\%$ vs. 5.67% , Fig. 3a and Table 1), which is opposite to the results for the hematite at pHs 6.5 and 7.5 (Fig. 3c and Table 1). Since dissolution of HANPs at acidic pH played appreciable roles in the cotransport of HANPs and goethite NPs in porous media (Wang et al., 2015a), the dissolution of HANPs in HANPs-hematite influents vs. pH was examined in batch experiments (see supplementary material Fig. S4). No detectable dissolution of HANPs was encountered when $\text{pH} \geq 7.5$, consistent with our recent findings (Wang et al., 2015a). In contrast, 4.4% HANPs was dissolved at pH 6.5, forming dissolved PO_4^{3-} ions. Therefore, the high breakthrough of HANPs obtained at pH 6.5 was due, in part, to the high mobility of dissolved PO_4^{3-} ions. Nevertheless, the limited dissolution (4.4%) of HANPs at pH 6.5 in batch system cannot completely account for the high mobility ($M_{\text{eff}} = 38.9\%$) of HANPs in column system. We anticipate that dissolution of HANPs is much greater in “dynamic” column system than in batch systems since dissolved PO_4^{3-} ion was progressively eluted out from the column. This is especially true when injecting pH 6.5 background electrolytes to dissolve retained HANPs (Wang et al., 2015a). In addition, homo-aggregation of HANPs is also likely to be weakened due to a decrease in overall collision efficiency since the HANPs were gradually dissolved in column system. Hence, enhanced dissolution of HANPs in “dynamic” column system and reduced homo-aggregation among HANPs populations are involved in the high mobility of HANPs at pH 6.5.

The RPs for both HANPs and hematite typically displayed a hyperexponential shape with greater retention in the column inlet (0–4 cm) and rapidly decreasing retention with depth (Fig.

3b, d), which is in contrast with CFT that predicts an exponential shape with depth (Yao et al., 1971). The hyperexponential RPs were less pronounced at higher pH. The D_H values of HANPs-hematite samples in the effluents and retentates are shown in Table 3. Irrespective of pH, the D_H value among the retentate reservoir decreased unidirectionally with increasing transport distance, i.e., from 0–4 cm. These observations are indicative of “size-selective retention” in porous media (Yao et al., 1971) with larger particles preferentially retained near the column inlet due to greater interception and sedimentation (Fig. 4) and smaller ones transported farther. The D_H values of effluent particles were substantially smaller than those of the retentates, further supporting that the size-selective retention occurred. The size-selective retention has been increasingly demonstrated to yield the hyperexponential RPs in NP transport studies (Jiang et al., 2012; Wang et al., 2012a; 2015a). Additionally, physical straining is also likely involved in the ripening BTCs and hyperexponential RPs for both HANPs and hematite at pHs 6.5 and 7.5 (Fig. 3), since the maximum values of D_H/d_{50} (i.e., 2.7×10^{-3} and 2.6×10^{-3} , respectively, at pHs 6.5 and 7.5) were larger than the threshold required for straining (2.0×10^{-3}) (Bradford et al., 2002).

In comparing the cotransport of HANPs and hematite with their individual transport at selected pH (see supplementary material Fig. S5), it is evident that greater mobility of HANPs (or hematite) occurred during cotransport at pH 10.5 (Fig. S5a, b). Since the maximum retention capacity of collector ($S_{\max}/C_o$) for both particles is limited at pH 10.5 (described above), competition for these favorable retention sites by negatively charged HANPs and hematite contributes to the higher mobility of both particles during their cotransport than individual transport. Similar findings were reported for the cotransport of bactericide and colloid (bismethiazol and montmorillonite colloid) (Shen et al., 2015) and NPs (C_{60} and TiO_2 NPs) (Cai et al., 2013) in saturated sand columns. Conversely, the addition of hematite in HANPs influent

inhibited the transport of HANPs at pH 7.5 and vice versa (Fig. S5c, d). This could be due to greater hetero-aggregation between HANPs and hematite in the influents at pH 7.5 compared to pH 10.5.

3.4.2. Effect of IS

Fig. 5 presents observed and fitted BTCs and RPs of HANPs and hematite, respectively, under different ISs (0.1, 10, and 50 mM KNO₃) at pH ~7.5 and $q = 0.44 \text{ cm min}^{-1}$ in the presence of 1 mg L⁻¹ SRHA. The transport of both particles decreased and retention increased with increasing IS, which are common observations in the transport of single-species colloid/NP in porous media (Chowdhury et al., 2011; Grolimund et al., 1998; Kretzschmar et al., 1997; Wang et al., 2014a; 2015b). These findings can be partly explained by enhanced particle aggregation (Table 3) and reduced electrosteric repulsion between particle-sand systems at higher ISs (supplementary material Fig. S3b). Moreover, nanoscale heterogeneity on collector surfaces is increasingly interpreted to play vital roles in colloids particularly NPs retention (Duffadar and Davis, 2008), which increases with increasing IS. Consequently, nanoscale heterogeneity is expected to cause more particle retention at higher ISs.

The shapes of BTCs and RPs for both particles displayed a transition from blocking to ripening (Fig. 5a, c) and from hyperexponential to flat (Fig. 5b, d), respectively, in response to increases in IS. The ripening BTCs observed for both HANPs and hematite indicate that 1 mg L⁻¹ SRHA cannot effectively stabilize the HANPs-hematite complexes at pH ~7.5 when IS ≥ 10 mM. Specifically, the D_H values of HANPs-hematite influents were 624 and 747 nm under KNO₃ concentrations of 10 and 50 mM, respectively, which were ~3 and 4-fold greater than that at 0.1 mM KNO₃ (181 nm) (Table 3). Close examination of the D_H values for HANPs-hematite

samples among the influent, effluent, and retentate reservoirs again reveals occurrence of sizeselective retention over the range of ISs considered (Table 3). Furthermore, this sizeselective retention became more pronounced at higher ISs, thereby yielding the more noticeable hyperexponential RPs at higher ISs (Jiang et al., 2012).

Previous studies indicated that the attractive secondary minimum region is likely involved in colloids/NPs retention particularly at higher ISs (Hahn and O'Melia, 2004; Tufenkji and Elimelech, 2005). Eluting the columns with DI water ($IS \approx 0$) after completion of the cotransport experiments released ~8.87 and 13.8% of the total injected HANPs, and ~2.65 and 4.92% of the total injected hematite under ISs of 10 and 50 mM KNO_3 , respectively (see supplementary material Fig. S6). These observations highlight that the secondary minimum is responsible for particle retention when IS was ≥ 10 mM. The mobility of HANPs was always less than that of hematite in the presence of 1 mg L^{-1} SRHA (Fig. 5 and Table 1). This is largely due to less sorption of negatively charged NOM onto negatively charged HANPs than to positively charged hematite (Tipping and Higgins, 1982), thereby resulting in less electrosteric repulsion to the HANPs relative to the hematite (Chen et al., 2012). Additionally, greater retention in the secondary minimum may also contribute to HANPs' lower mobility of compared to hematite.

The BTCs for cotransport and individual transport of HANPs and hematite when SRHA = 1 mg L^{-1} under ISs of 10 and 50 mM are shown in the supplementary material Fig. S7. The individual transport of HANPs and hematite was much greater than their cotransport particularly at a higher IS (50 mM KNO_3), consistent with the results obtained at pH 7.5 (Fig. S5c, d). Nonetheless, ripening still occurred for the individual transport of HANPs when SRHA = 1 mg L^{-1} and $IS \geq 10$ mM (Fig. S7a, c), indicating that 1 mg L^{-1} SRHA cannot stabilize the HANPs at high ISs (≥ 10 mM). Conversely, blocking were observed for the individual transport of hematite

when SRHA = 1 mg L⁻¹ at ISs of 10 and 50 mM, mirroring the pivotal role of HANPs in weakening the transport of hematite even in the presence of SRHA.

The ripening model provided a good description for the BTCs and RPs of both particles under ISs of 10 and 50 mM KNO₃ (Fig. 5 and Table 4). The values of k_{int} and k_{d} for HANPs and hematite were much greater than those of k_{r} , suggesting that interaction and deposition of particles determine their mobility, as observed at low pH tests (6.5 and 7.5). The value of k_{d} was greater and the value of k_{r} was lower at a higher IS, meaning that particle deposition depends on the attractive interaction (e.g., nanoscale heterogeneity of collector and secondary minimum), which increases with increasing IS.

3.4.3. Effect of flow rate

To determine the role of hydrodynamics on the cotransport and retention of HANPs and hematite, experiments were conducted under different Darcy velocities ($q = 0.44, 0.22, \text{ and } 0.044$ cm min⁻¹) at pH 7.5 and IS = 0.1 mM KNO₃ (Fig. 6). Higher mass effluent recovery and less retention were encountered for both particles at higher q , which is in agreement with published results (Chowdhury et al., 2011; Grolimund et al., 1998; Harter et al., 2000; Kretzschmar et al., 1997; Li et al., 2008; Wang et al., 2012b; 2014a). The ripening BTCs and hyperexponential RPs observed at varying q indicate that homo-aggregation and hetero-aggregation of HANPs and hematite determine their mobility (described above). Consistent with the trends obtained at different pHs and ISs, the individual transport of HANPs and hematite was always greater than their cotransport, as shown in the supplementary material Fig. S8. These observations again support the fact that hetero-aggregation between negatively charged HANPs and positively charged hematite at pH ~7.5 weakens the mobility of both particles. Comparison of the D_{H}

values of HANPs-hematite samples in the influents, effluents, and retentates reveals that particle aggregation and sizeselective retention were more pronounced at lower q (Table 3), which accounts for the more significant ripening and hyperexponential RPs at lower q . The ripening BTCs occurred for both the co- and individual-transport of HANPs and hematite, indicating that the mobility of both particles is very limited in the absence of NOM, even when IS was as low as 0.1 mM KNO₃ (pH ~7.5).

The ripening model again well approximated the BTCs and RPs of both HANPs and hematite at different q (Fig. 6 and Table 4). Consistent with the results attained at low pH tests (6.5 and 7.5), the values of k_r were 2–3 orders of magnitudes smaller than those of k_{int} and k_d , indicative of the insignificant role of particle release (i.e., irreversible retention). The CFT (Yao et al., 1971) predicts that the value of k_d is proportional to q raised to the 1/3 power (Schijven and Hassanizadeh, 2000). Nonetheless, the overall rate of advection is proportional to q such that a systematic decrease in particle retention is anticipated with an increase in q . The observed k_d trends for both HANPs and hematite are therefore consistent with the CFT prediction (Table 4). Similarly, the absolute values of k_{int} also increased with increasing q , consistent with the trend for the k_d . This finding reflects that HANPs-hematite interaction is dependent on q and increases with increasing q .

3.5. Phosphate oxygen isotope ratios of HANPs and isotopic fractionation

3.5.1. IS effect

To assess the role of environmentally relevant IS on phosphate oxygen isotope fractionation among HANPs populations during cotransport, selected HANPs-hematite samples in the influents, effluents, and retentates recovered at ISs of 10 and 50 mM KNO₃ in the presence

of 1 mg L⁻¹ SRHA were individually processed to quantify their O-isotopic composition. The IS
 was found to exert a marked impact on the isotope fractionation of HANPs (Fig. 7). Regardless of
 IS, the $\delta^{18}\text{O}_\text{P}$ values of HANPs among the influent, effluent, and retentate reservoirs followed the
 order: effluent > influent > retentate. For the effluent reservoir, the $\delta^{18}\text{O}_\text{P}$ values decreased with
 eluted PV and tended to approach the influent $\delta^{18}\text{O}_\text{P}$ values (10.70‰). Similarly, this isotopic
 fractionation between retentates and influents became less significant at greater depths (e.g.,
 from 1–5 cm). This fractionation was more prominent at a higher IS (i.e., 50 mM KNO₃). For
 instance, at IS = 10 mM KNO₃, the O-isotopic fractionation between effluents and influents at
 the early stage of transport (i.e., 2 PV) was ~0.82‰, whereas the difference was ~1.32‰ when
 IS = 50 mM KNO₃ (Fig. 7). A similar trend was obtained between influents and retentates at the
 tested ISs. These findings are in close agreement with a recent study (Jaisi, 2013) in which
 isotope fractionation of dissolved PO₄³⁻ ion was examined at different ISs and flow rates.
 Specifically, at $q = 0.0049 \text{ cm min}^{-1}$ over a wide range of ISs (1–100 mM KCl), the isotope
 fractionation between the effluent and influent phosphates at the initial stage (i.e., 2 PV) was
 ~1.10% with isotopically-heavier phosphates (P¹⁸O₄) preferentially passed through the column
 packed with natural sediments because the lighter phosphates (P¹⁶O₄) were thermodynamically
 favorably retained (sorbed) by the sediments (Jaisi, 2013; Jaisi et al., 2010). It was further
 pointed that this isotopic fractionation decreased gradually and became insignificant as more
 phosphates passed through the column due to efficient ion exchange between aqueous and
 retained (sorbed) phosphates (Jaisi, 2013; Jaisi et al., 2010). The ion exchange effect has long
 been proposed to interpret the isotopic fractionation between dissolved ion and solid mineral,
 such as Fe isotope fractionation between aqueous Fe^{2+/3+} ion and iron oxide minerals (e.g.,
 ferrihydrite, goethite, hematite, and magnetite) (Beard et al., 1999; Cwiertny et al., 2008; Gorski

et al., 2012; Skulan et al., 2002). However, in this study, the ion exchange is unlikely to account for the isotope fractionation of HANPs obtained at ISs of 10 and 50 mM KNO₃ (pH ~7.5) since no dissolution of HANPs occurred (see supplementary material Fig. S4).

Given that the particles including NPs are expected to behave differently than the dissolved ions, there should be other different mechanism/s governing the isotope fractionation of HANPs during transport. Since particle aggregation is apparent particularly at higher ISs (Table 3), it is intuitive to assume that particle aggregation could be a plausible mechanism responsible for the isotopic fractionation at varying ISs (Fig. 7). This is because the aggregation is a diffusion-controlled reaction, which is analogous to the reactions of nucleation and Ostwald ripening during crystal growth processes that commonly yield non-equilibrium and kinetic isotopic fractionation (Guilbaud et al., 2010; Steefel and Van Cappellen, 1990; Stoffregen, 1996; Watson and Muller, 2009). The origin of the primary driving force for nucleation and Ostwald ripening lies in the interfacial free energy of a mineral, which involves a redistribution (e.g., dissolution and then reprecipitation) of mass from small particles to large particles in the system (Steefel and Van Cappellen, 1990; Stoffregen, 1996). That is, an increase in average particle size and a decrease in the number of particles with time thermodynamically occur due to a net transfer of material from small to large particles (the overall reactive surface area diminishes correspondingly) (Steefel and Van Cappellen, 1990; Stoffregen, 1996; Waychunas et al., 2005). In particular, Guilbaud et al. (2010) found that the Fe isotope fractionation between aqueous Fe²⁺ ion and nanoparticulate mackinawite (FeS) was up to 1.17‰ at 25 °C, which is interpreted by particle aggregation. All these interpretations reflect that the isotope fractionation of HANPs during transport is most likely initiated by particle aggregation. Theoretically, the hetero-aggregation between isotopically-lighter HANP (i.e., P¹⁶O₄) and hematite is more

thermodynamically favored than the heavier HANP analogue (e.g., $P^{18}O_4$) due to lower enthalpy and interfacial free energy of the lighter one compared to the heavier one (Navrotsky et al., 2008; Steefel and Van Cappellen, 1990; Waychunas et al., 2005). Since the sizeselective retention occurs during HANPs transport at various ISs (Table 3), the HANPs with isotopically-light phosphates (i.e., $P^{16}O_4$) are expected to preferentially hetero-aggregate with hematite and deposit gradually along the column profile, whereas those with heavy phosphates (i.e., $P^{18}O_4$) hetero-aggregate slowly and ultimately elute from the column, which results in the retentates and effluents enriching in $P^{16}O_4$ and $P^{18}O_4$, respectively. In addition, particle aggregation in the retentate reservoir was less pronounced at greater depths (Table 3), which likely accounts for the smaller isotopic fractionation between retentates and influents at greater depths (Fig. 7). Similarly, the isotopic fractionation was less significant at lower ISs, likely attributable to the less sizeselective retention of HANPs during transport (Table 3).

3.5.2. Flow rate effect

The flow rate was recently found to exert a marked influence on the isotope fractionation of dissolved PO_4^{3-} ion in saturated sediment columns (Jaisi, 2013). Our data also demonstrate that the isotope fractionation of HANPs was also dependent on the flow rate (Fig. 8). Again, the $\delta^{18}O_P$ values of HANPs were in the following order of effluent > influent > retentate, irrespective of flow rate. At $q = 0.44 \text{ cm min}^{-1}$, the O-isotopic composition in the retentate reservoir became gradually heavier at greater depths (e.g., from 1–4 cm), consistent with the results obtained at different ISs. This is likely due to less aggregation of HANPs at greater depths, as described above (Table 3). The isotopic fractionation decreased progressively and became insignificant with decreasing q . For example, at the depth of 1 cm, the $\delta^{18}O_P$ values of retentate increased

from 9.73 to 10.46, and then to 10.57‰ when q was decreased from 0.44 to 0.22, and then to 0.044 cm min⁻¹, respectively (Fig. 8). Similarly, with decreasing q , the $\delta^{18}\text{O}_\text{P}$ values in the effluent reservoir became progressively lighter, consistent with previously documented results (Jaisi, 2013). A conceptual diagram (supplementary material Fig. S9) is used to illustrate the role of flow rate on the isotopic fractionation effect. It is logical to anticipate that the isotope fractionation among HANPs populations during transport lies in the falling limb of the curve shown in Fig. S9, because most of the HANPs ($\geq 93.3\%$, Table 1) were retained in the column at different q . Larger isotopic fractionation occurs at higher q due to greater mass transfer of HANPs between the influents and effluents (i.e., less particle aggregation, see Table 3). As q decreases, this isotopic fractionation is erased and appears to approach equilibrium due to less mass transfer between the influents and effluents. It should be mentioned that the isotope fractionation of HANPs between effluent and influent reservoirs was $\sim 2.02\%$ at $q = 0.44$ cm min⁻¹ (Fig. 8), which is 0.72% heavier than the one ($\sim 1.30\%$) observed by Jaisi (2013). This is partly because the q used in our study is >15 -fold greater than the one (0.029 cm min⁻¹) employed by Jaisi (2013). An alternative explanation for this disparity is that NPs may hold distinct isotopic properties from their bulk or dissolved counterparts (Cwiertny et al., 2008; Navrotsky et al., 2008; Waychunas et al., 2005). For example, the heterogeneities of NPs (e.g., size, shape, anisotropy, surface chemistry, and structural density) (Shevchenko et al., 2006) are significantly greater than those of homogeneously dissolved ions, which likely affect the reactivity of NPs more than dissolved ions. Additional research is needed to fully resolve this issue but is beyond the scope of the current study.

4. Conclusions

Column experiments were designed to elucidate the cotransport and retention of HANPs and hematite at various pHs, ISs, and flow rates. Our results demonstrated that the cotransport and retention of HANPs and hematite are highly sensitive to the physicochemical factors considered. The mobility of HANPs and hematite during cotransport increased with increasing pH and flow rate, and decreasing IS. Nevertheless, the mobility of both HANPs and hematite was substantially lower during cotransport than their individual transport, primarily due to greater aggregation of HANPs, hematite, and HANPs-hematite complexes when both particles were copresent in the suspension. During cotransport, the shape of BTCs and RPs for both particles frequently transformed from blocking to ripening with time and from flat to hyperexponential with depth, respectively, in response to variability in the tested physicochemical factors. A one-site kinetic attachment model can adequately capture the main features of the blocking BTCs and RPs that are hyperexponential or flat, whereas a ripening model that includes attractive particle-particle interaction has to be employed to simulate the ripening BTCs. Model-fitted parameters exhibited systematic trends with tested experimental conditions.

For the first time, the phosphate oxygen isotope fractionation among HANPs populations during cotransport was explored under various ISs and flow rates. A small isotopic fractionation occurred ($\leq 2\%$) between effluent and influent and between retentate and influent, mostly likely initiated by hetero-aggregation between HANPs and hematite. Furthermore, this isotopic fractionation became more pronounced at higher ISs due to enhanced aggregation. Larger isotopic fractionation was obtained at a higher flow rate, but this fractionation was decreased with decreasing flow rate due to less mass transfer between influent and effluent HANPs. To

date, accurate detection and characterization of NPs in complex subsurface environments are still rather challenging. Given that different sources of phosphate-based NPs may hold distinct $\delta^{18}\text{O}_\text{P}$ signatures, and the transport-related isotope fractionation is insignificant, isotope tracing could serve as a promising tool to identify the sources and transport of phosphate-based NPs in complex subsurface environments.

Supplementary material

Supplementary material includes determination of the concentration of hematite stock suspension (S1), preparation of Suwannee River humic acid stock solution (S2), DLVO interaction energy calculation (S3), and Figures S1–S9.

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Table 1. Physicochemical properties and mass recovery percentages for column experiments under different experimental conditions.

pH	IS ^a (mM)	q^b (cm min ⁻¹)	SRHA ^c (mg L ⁻¹)	Recovery (%)					
				HANPs			Hematite		
				M_{eff}^d	M_{ret}^e	M_{tot}^f	M_{eff}^d	M_{ret}^e	M_{tot}^f
6.5	0.1	0.44		38.9	55.0	93.9	2.65	108	111
7.5	0.1	0.44		5.67	93.3	99.0	3.77	97.5	101
10.5	0.1	0.44		93.2	13.8	107	89.0	9.30	98.3
7.5	0.1	0.44	1	77.8	5.27	83.1	97.1	1.13	98.2
7.6	10	0.44	1	42.1	55.4	97.5	62.4	35.4	97.8
7.6	50	0.44	1	11.1	88.1	99.2	11.3	86.5	97.8
7.5	0.1	0.22		2.54	99.9	102	1.53	100	102
7.5	0.1	0.044		1.15	108	109	0.38	101	101

^aIonic strength. ^b Darcy velocity. ^cSuwannee River humic acid. ^{d, e, and f} Effluent, retentate, and total percentages of HANPs (or hematite) recovered from column experiments, respectively.

Table 2. Electrokinetic properties of HANPs-hematite influents, quartz sands, and individual HANPs suspensions under different experimental conditions.

pH	IS (mM)	q (cm min ⁻¹)	SRHA (mg L ⁻¹)	Zeta potential (mV)		
				$\zeta_{\text{influent}}^a$	ζ_{sand}^b	ζ_{HANPs}^c
6.5	0.1	0.44		0.32 ± 0.13 a	-20.7 ± 1.2 a	-22.1 ± 0.78 a
7.5	0.1	0.44		-3.21 ± 0.66 b	-21.3 ± 1.4 a	-26.3 ± 0.59 b
10.5	0.1	0.44		-23.1 ± 2.4 c	-43.6 ± 1.2 b	-31.1 ± 1.6 c
7.5	0.1	0.44	1	-15.6 ± 2.5 a	-25.3 ± 2.1 a	-29.6 ± 0.83 a
7.6	10	0.44	1	-11.1 ± 1.1 b	-15.3 ± 0.81 b	-25.1 ± 1.0 b
7.6	50	0.44	1	-5.72 ± 0.15 c	-4.37 ± 1.8 c	-18.9 ± 0.75 c
7.5	0.1	0.22		-3.21 ± 0.66 b	-21.3 ± 1.4 a	-26.3 ± 0.59 b
7.5	0.1	0.044		-3.21 ± 0.66 b	-21.3 ± 1.4 a	-26.3 ± 0.59 b

^a, ^b, and ^c ζ -potentials of HANPs-hematite influents, quartz sands, and individual HANPs suspensions, respectively. Mean values ± standard deviations in each vertical column followed by the same lowercase letters are not significantly different using Tukey's HSD test at $p < 0.05$.

Table 3. Average hydrodynamic diameters (D_H) of HANPs-hematite samples in the influents, effluents, and retentates in the column at different depths, and D_H of individual HANPs under different experimental conditions.

pH	IS (mM)	q (cm min ⁻¹)	SRHA (mg L ⁻¹)	D_H of HANPs-hematite sample (nm)						D_H of HANPs (nm)
				Influent	Effluent	Retentate (nm)				
						0–1	1–2	2–3	3–4	
6.5	0.1	0.44		1283 ± 248 a	669 ± 46 a	1863 ± 81 a	1473 ± 103 a	1406 ± 379 a	742 ± 189 a	1021 ± 192 a
7.5	0.1	0.44		958 ± 263 b	675 ± 72 a	1776 ± 111 a	1402 ± 157 a	1269 ± 43 a	758 ± 32 a	907 ± 80 a
10.5	0.1	0.44		635 ± 101 c	220 ± 10 b	1323 ± 115 b	827 ± 174 b	537 ± 114 b	310 ± 31 b	274 ± 12 b
7.5	0.1	0.44	1	181 ± 17 a	180 ± 3.6 a	437 ± 188 a	403 ± 142 a	335 ± 67 a	342 ± 41 a	272 ± 14 a
7.6	10	0.44	1	624 ± 24 b	473 ± 41 b	823 ± 36 b	693 ± 42 b	601 ± 139 b	641 ± 34 b	324 ± 13 b
7.6	50	0.44	1	747 ± 149 bc	616 ± 70 c	945 ± 22 c	703 ± 35 b	723 ± 56 b	604 ± 85 b	452 ± 30 c
7.5	0.1	0.22		958 ± 263 b	890 ± 55 b	1884 ± 81 a	1442 ± 54 a	1351 ± 38 b	809 ± 85 ab	907 ± 80 a
7.5	0.1	0.044		958 ± 263 b	1033 ± 64 c	1843 ± 38 a	1474 ± 44 a	1041 ± 49 c	680 ± 72 ab	907 ± 80 a

Mean values ± standard deviations in each vertical column followed by the same lowercase letters are not significantly different using Tukey's HSD test at $p < 0.05$.

Table 4. Fitted model parameters for the cotransport of HANPs and hematite, respectively, in column experiments under different experimental conditions using the one-site kinetic attachment model or the ripening model.

pH	IS (mM)	q (cm min ⁻¹)	SRHA (mg L ⁻¹)	HANPs						Hematite							
				One-site model			Ripening model			R^{2g}	One-site model			Ripening model			R^2
				$S_{\max}/C_o^a$	k_a^b	β^c	k_{int}^d	k_d^e	k_r^f		$S_{\max}/C_o$	k_a	β	k_{int}	k_d	k_r	
6.5	0.1	0.44		5.31	1.96	0.659				0.858				-0.228	0.470	2.68E-4	0.966
7.5	0.1	0.44					-0.208	0.437	4.88E-3	0.920				-0.248	0.407	3.51E-4	0.990
10.5	0.1	0.44		0.560	76.9	2.28				0.963	0.221	31.2	1.69				0.955
7.5	0.1	0.44	1	0.183	25.5	1.33				0.915	5.87E-2	7.94	0.764				0.955
7.6	10	0.44	1				-0.232	9.22E-2	5.39E-3	0.943				-0.272	4.04E-2	6.84E-3	0.932
7.6	50	0.44	1				-0.135	0.326	3.43E-3	0.999				-0.121	0.314	2.27E-3	1.00
7.5	0.1	0.22					-3.78E-2	0.271	1.61E-4	0.907				-0.137	0.270	1.17E-4	0.994
7.5	0.1	0.044					-5.11E-3	6.90E-2	3.95E-5	0.937				-5.54E-2	6.96E-2	4.29E-5	0.994

^a Normalized maximum solid-phase concentration of retained particles [cm³ g⁻¹]. ^b First-order attachment rate coefficient [min⁻¹]. ^c An empirical parameter controlling the shape of the spatial distribution of retained particles [-]. ^d Particle interaction rate coefficient [cm³ min⁻¹ N⁻¹]. ^e Particle deposition rate coefficient [min⁻¹]. ^f Particle release rate coefficient [min⁻¹]. ^g Squared Pearson's correlation coefficient.

Fig. 1. Powder XRD pattern (a), FTIR spectrum (b), SEM image (c), and TEM image (d) of the hematite. The scale bars in (c, d) are 100 and 500 nm, respectively.

Fig. 2. TEM images of the HANPs-hematite influent at pH 7.5. The scale bar in (a, b) is 100 nm.

At pH 7.5, the negatively charged HANPs readily sorb onto the positively charged hematite via electrostatic attraction.

Fig. 3. pH effect: observed and fitted cotransport breakthrough curves (a, c) and retention profiles (b, d) of HANPs (a, b) and hematite (c, d), respectively, at varying pHs (6.5, 7.5, and 10.5) when $IS = 0.1 \text{ mM KNO}_3$ and $q = 0.44 \text{ cm min}^{-1}$. Note different scales in y-axes. The blocking breakthrough curves were simulated using the one-site kinetic attachment model, whereas the ripening model was used to fit the ripening breakthrough curves.

Fig. 4. (a, b) SEM images of HANPs aggregates, hematite aggregates, and HANPs-hematite complexes retained on the sand grains that were excavated from the column inlet (0–1 cm) after completion of the cotransport of HANPs and hematite at pH 7.5, IS = 0.1 mM KNO₃, and $q = 0.44 \text{ cm min}^{-1}$. (c) The corresponding energy-dispersive X-ray (EDX) spectrum of the retained HANPs-hematite complexes (b) on the sand grain based upon the line scanning technique. The scale bars in (a, b) are 200 and 500 nm, respectively.

Fig. 5. IS effect: observed and fitted cotransport breakthrough curves (a, c) and retention profiles (b, d) of HANPs (a, b) and hematite (c, d), respectively, under ISs of 0.1, 10, and 50 mM KNO_3 in the presence of 1 mg L^{-1} SRHA at pH ~ 7.5 and $q = 0.44 \text{ cm min}^{-1}$.

Fig. 6. Flow rate effect: observed and fitted cotransport breakthrough curves (a, c) and retention profiles (b, d) of HANPs (a, b) and hematite (c, d), respectively, under q of 0.44, 0.22, and 0.044 cm min⁻¹ at pH 7.5 and IS = 0.1 mM KNO₃.

Fig. 7. Effect of IS on isotope fractionation: shown are the $\delta^{18}\text{O}_P$ values of HANPs in the influent, effluent (e.g., 2, 4, and 6 PV), and retentate samples at different depths (e.g., 1, 5, and 2–10 cm) at two ISs, 10 and 50 mM KNO_3 , respectively. All column experiments were conducted at pH ~ 7.5 and $q = 0.44 \text{ cm min}^{-1}$ in the presence of 1 mg L^{-1} SRHA. The $\delta^{18}\text{O}_P$ value of the HANPs starting (influent) suspension was 10.70‰ (shown by the dotted line). Standard deviation was calculated using $\delta^{18}\text{O}_P$ values obtained from independent column experiments. The solid lines are the trends of isotope fractionation but not fitting results.

Fig. 8. Effect of flow rate on isotope fractionation: shown are the $\delta^{18}\text{O}_P$ values of HANPs in the influent, effluent, and retentate samples at different depths (e.g., 1, 2, 3, and 4 cm) at q of 0.44, 0.22, and 0.044 cm min⁻¹, respectively. All column experiments were performed at pH 7.5 and IS = 0.1 mM KNO₃. The $\delta^{18}\text{O}_P$ value of the HANPs starting (influent) suspension was 10.70‰ (shown by the dotted line). Standard deviation was calculated using $\delta^{18}\text{O}_P$ values obtained from independent column experiments. The solid lines are the trends of isotope fractionation but not fitting results. At $q = 0.44$ cm min⁻¹, the O-isotopic composition in the retentate became gradually heavier at greater depths (e.g., from 1 to 4 cm). Similarly, for the retentate at 1 cm depth, the $\delta^{18}\text{O}_P$ value increased with decreasing q (from 0.44 to 0.044 cm min⁻¹). In contrast, with decreasing q , the $\delta^{18}\text{O}_P$ value of effluent decreased.