Cotransport of hydroxyapatite nanoparticles and hematite colloids in saturated porous media: Mechanistic insights from mathematical modeling and phosphate oxygen isotope fractionation

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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 (≤1.8‰) 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.

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, $Ca_{10}(PO_4)_6(OH)_2$) have been employed in the medical field 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 Lal, 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 ($Ca(H_2PO_4)_2$). 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; Grolimund 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 enzyme causes changes in isotopic composition (Blake et al., 1997; Liang and Blake, 2006, 2009; Paytan et al., 2002; Stout et al., 2014). Interestingly, in abiotic systems, oxygen isotope exchange is insignificant between phosphate and ambient water at low temperature (<80 °C) and near-neutral pH conditions (Jaisi et al., 2010; Lecuyer et al., 1999; Li and Jaisi, 2015). More extensive application of oxygen isotope ratios in phosphate ($\delta^{18}O_P$) as a biogeochemical tracer of P sources and cycles, however, relies on a more complete understanding of all processes and reactions that could (or not) lead to changes of isotopic compositions as well as fractionation factors for particular reactions or processes. To date, there is just one study aimed at elucidating the isotope effects during phosphate transport in the subsurface environments (Jaisi, 2013), thus limits our ability to better predict the variability of $\delta^{18}O_P$ values between subsurface soils and pore-water. Jaisi (2013) found that oxygen isotope exchange of dissolved phosphate ion between the effluent and influent was ~1.3‰ with isotopically-lighter phosphate ($P^{16}O_4$) preferentially retained in the column in the early stage of transport, and this isotopic fractionation became negligible as more phosphate passed through the column due to the efficient exchange between aqueous and sorbed phosphate ions over time. However, the physical and thermodynamic properties of NPs are different from ions, and the extent of isotope effects of NPs during transport is therefore