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Facilitated transport of Cu with hydroxyapatite nanoparticles in saturated sand: Effects of solution ionic strength and composition

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ARTICLE INFO

Article history:
Received 2 May 2011
Received in revised form
23 August 2011
Accepted 24 August 2011
Available online 16 September 2011

Keywords:
Hydroxyapatite nanoparticles (nHAP)
Cu
nHAP-facilitated Cu (nHAP-F Cu)
Co-transport
Ionic strength (IS)
Ionic composition (IC)

ABSTRACT

Column experiments were conducted to investigate the facilitated transport of Cu in association with hydroxyapatite nanoparticles (nHAP) in water-saturated quartz sand at different solution concentrations of NaCl (0–100 mM) or $CaCl_2$ (0.1–1.0 mM). The experimental breakthrough curves and retention profiles of nHAP were well described using a mathematical model that accounted for two kinetic retention sites. The retention coefficients for both sites increased with the ionic strength (IS) of a particular salt. However, the amount of nHAP retention was more sensitive to increases in the concentration of divalent Ca^{2+} than monovalent Na^{+}. The effluent concentration of Cu that was associated with nHAP decreased significantly from 2.62 to 0.17 mg L^{-1} when NaCl increased from 0 to 100 mM, and from 1.58 to 0.16 mg L^{-1} when $CaCl_2$ increased from 0.1 to 1.0 mM. These trends were due to enhanced retention of nHAP with changes in IS and ionic composition (IC) due to compression of the double layer thickness and reduction of the magnitude of the zeta potentials. Results indicate that the IS and IC had a strong influence on the co-transport behavior of contaminants with nHAP nanoparticles.

1. Introduction

Nanotechnology focuses on the investigation and application of materials with at least one characteristic dimension less than 100 nm. Properties of nanomaterials such as small size, high surface area per unit volume and great reactivity make them a highly promising class of materials for a variety of potential applications. For example, hydroxyapatite nanoparticles

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0043-1354/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2011.08.041

($Ca_{10}(PO_4)_6(OH)_2$, nHAP), which are the main component of hard tissues of vertebrates such as bones and teeth, have been widely applied for the remediation of contaminated soil and purification of wastewaters polluted by metal ions and actinides (Cu^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, and Sr^{2+}) because of their strong ability to fix them (Ma et al., 1994; Smiciklas et al., 2006; Handley-Sidhu et al., 2011). The fixation of metal ions on nHAP may take place through one or more mechanisms, including: ion exchange, surface complexation, and dissolution of nHAP to form new metal phosphates (Ma et al., 1994; Smiciklas et al., 2006; Handley-Sidhu et al., 2011).

To date, little attention has been paid to potential environmental risks of using nHAP to remediate soils contaminated by heavy metals. Specifically, nHAP may alter the transport and fate of common environmental metal contaminants, such as Cu, by dramatically affecting their distribution among mobile and immobile phases (Wang et al., 2011). The transport potential of many chemicals is known to be greatly enhanced when they are associated with mobile colloids (McCarthy and Zachara, 1989; de Jonge et al., 2004; Simunek et al., 2006; Bradford and Kim, 2010). This process is often referred to as "colloid-facilitated contaminant transport" (Grolimund et al., 1996; Roy and Dzombak, 1997). Colloid-facilitated contaminant transport in subsurface environments has attracted considerable attention in recent years, especially for nanoscale colloids such as buckminsterfullerene (Zhang et al., 2011) and TiO_2 (Fang et al., 2011). However, essentially no published data are available on how nHAP might mediate the transport and fate of Cu in subsurface environments.

The solution ionic strength (IS) and composition (IC) are known to have a large influence on the transport behavior of colloid-associated contaminants. For example, Cheng and Saiers (2010) reported that the capacity of sediment-colloids to bind ^{137}Cs decreased with increasing IS (Na^+ cation), leading to a decrease of the mass of ^{137}Cs eluted from columns packed with Hanford coarse sand. Walshe et al. (2010) found that increasing the IS (Ca^{2+} cation) of the bulk solution reduced peak concentrations for both kaolinite and kaolinite-facilitated MS2 coliphage from columns composed of gravel aquifer media. The influence of IS and IC on colloid and nanoparticles interactions with solid surfaces is typically explained using theory developed by Derjaguin–Landau–Verwey–Overbeek (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). This theory predicts that increasing the solution IS tends to decrease the double layer thickness and magnitude of the surface charge, and thereby increase colloid retention. Divalent ions have a greater effect on these properties than monovalent ions (Israelachvili, 1992; Elimelech et al., 1995). However, up till now there has been no systemic investigation concerning the effects of IS on the co-transport behavior of Cu with nHAP. Furthermore, divalent Ca^{2+} can compete with Cu for ion-exchange sites of nHAP, leading to enhance dissociation of Cu^{2+} from nHAP, and thus altering the co-transport behavior of Cu with nHAP. It is therefore crucial to investigate the impact of the divalent Ca^{2+} on the co-transport behavior of Cu with nHAP in saturated packed columns. The overall objective of this study was to systemically investigate the effects of solution IS and IC on the co-transport of Cu with nHAP.

2. Materials and methods

2.1. Quartz sand

Quartz sand (Sinopharm Chemical Reagent Co., Ltd., China) was used as column packing material. The grain size distribution of the sand was determined by sieve analysis. The median grain size (d_{50}) of the sand was 600 μm, and the coefficient of uniformity ($U_i = d_{60}/d_{10}$ where x% of the mass was finer than d_x) was 1.3. Prior to use, the sand was cleaned thoroughly by the procedure described elsewhere (Zhou et al., 2011) to remove any metal oxide and absorbed clay on the sand surface. The ζ-potential of the quartz colloid was measured by the method described in our previous work (Wang et al., 2011; Zhou et al., 2011).

2.2. nHAP

The nHAP used in this study (purity >99.9%) was purchased from Aipurui Nanomaterial Company (Nanjing, China). The physicochemical properties of the nHAP were determined in our previous work (Wang et al., 2011). Briefly, the nHAP particles are rod-shaped and their mean size is 20 nm in width and 100 nm in length, the Ca/P molar ratio is 1.65 and the specific surface area of the nHAP is 154 $m^2\ g^{-1}$.

2.3. Co-transport tests

Cleaned quartz sand was dry-packed into a glass chromatographic column (20 cm × 2.6 cm, Shanghai, China) with 80 μm stainless-steel screens on both ends. Each column contained approximately 150 g of quartz sand and had an average length of 20 cm. To achieve uniform packing, the sand was carefully added to the column using a spatula and then gently vibrated. The column was slowly saturated by pumping ultrapure water (18.2 MΩ, Millipore, Inc., USA) in the upward direction at an approach velocity of 0.1 cm min^{-1} for 1 h. Following this saturated step, the water content of each column was determined gravimetrically. The porosity of the packed columns varied between 0.39 and 0.41. Table 1 shows the most salient properties of the packed columns used in the co-transport tests of nHAP. The longitudinal dispersivity of the packed column was estimated from transport tests using bromide as tracer.

Table 1 – Properties and parameters of the nHAP and packed quartz sand columns used in this study.

nHAP length (L) nm	100
nHAP width (L) nm	20
nHAP density (ρ_n) g cm^{-3}	3.2
Collector diameter (d_c) mm	0.6
Fluid density (ρ_f) kg m^{-3}	10^3
Fluid viscosity (μ) kg m^{-1} s^{-1}	8.9×10^{-4}
Temperature (T) K	293
Hamaker constant (A) J	1.0×10^{-20}
Porosity (f) cm^3 cm^{-3}	0.39–0.41
Column length (L) cm	20.0
Column diameter (L) cm	2.6
Happel model parameter (A_s)	36.1–41.2