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Transport behavior of humic acid-modified nano-hydroxyapatite in saturated packed column: Effects of Cu, ionic strength, and ionic composition

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ABSTRACT

The surfaces of nano-hydroxyapatite (nHAP) used for contaminated soil and groundwater remediation may be modified to render nHAP highly mobile in the subsurface. Humic acid (HA) is widely used to modify and stabilize colloid suspensions. In this work, column experiments were conducted to determine the effects of contaminant (e.g., Cu) concentration, ionic strength (IS), and ion composition (IC) on the transport behavior of HA-modified nHAP in saturated packed columns. IS and nature of the cation had strong effects on the deposition of nHAP, and the effect was greater for divalent than for monovalent cations. Divalent cations have a greater capacity to screen the surface charge of nHAP, and Ca^{2+} bridges the HA-modified nHAP colloidal particles, which causes greater deposition. Moreover, Cu^{2+} had a greater effect on the transport behavior than Ca^{2+} due to their strong exchange with Ca^{2+} of nHAP and its surface complexation with nHAP. The relative travel distance L_T, of the injected HA-modified nHAP colloids, ranges from less than one to several meters at varying Cu concentrations, ISs, and ICs in saturated packed columns. The results are crucial to evaluate the efficacy of nHAP on the remediation of contaminated soil and groundwater environments.

1. Introduction

Nanotechnology focuses on the investigation and application of materials with at least one characteristic dimension less than 100 nm [1]. The properties of nanomaterials such as small size, high surface area, low density, and high surface to volume ratio make them a highly promising novel class of materials for a variety of potential applications. Nano-hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, nHAP), which is the main component of hard tissues of vertebrates such as bones and teeth, for example, has significant potential in the field of orthopedics, dentistry, and drug delivery [2–4]. In the environmental science and engineering community, it has been widely applied for the remediation of contaminated soil [5–7] and purification of wastewaters polluted by heavy metals for its strong ability to fix heavy metals [8–10]. Metal ions such as Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Co^{2+} were successfully stabilized in contaminated soil or removed from wastewater through coprecipitation with nHAP by means of ion exchange, surface complexation, and dissolution of nHAP to form new metal phosphates [6,7,8–10].

Natural organic matters (NOMs) such as HA and fulvic acid (FA), present in the soil solutions and groundwater environments, are one of the key factors governing the environmental transport and fate of colloids. NOMs can be adsorbed onto colloidal particles, altering their surface properties, and consequently affecting their transport patterns. In previous work, we demonstrated that the nHAP exhibited limited transport in the absence of HA because of its high aspect ratio and high surface area. However, its transport capacity was significantly enhanced by the presence of HA in the bulk solution in saturated sand columns [11]. It is generally accepted that HA adsorbed on the surface of colloidal particles can stabilize the colloidal particles due to the existence of both electrostatic repulsion and steric hindrance effects [12,13]. nHAP has been widely used for the remediation of contaminated soil and groundwater environments, typically comprising a large amount of HA. HA was therefore selected as a modifier to stabilize nHAP colloidal suspensions to simulate a more realistic subsurface environment in the present study.

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The most of the surfaces in natural porous media, minerals, and soil organic matter possess a negative surface charge at the prevailing pH conditions, thus leading to unfavorable attachment conditions [14,15], although the source of the negative electrokinetic potential of the nHAP colloid is still not understood [16]. The effects of solution chemistry such as IS and IC (mono- and divalent cations) governing the fate and transport behavior of nanomaterials such as nanoscale zerovalent iron [17] and fullerene (C_{60}) [18] in porous media have been studied extensively. The expected effect – increased deposition at higher IS or in the presence of divalent cation in the bulk solution – is attributed to decreasing of repulsive surface interaction energies between colloids, and colloids and grain surfaces [19], which is in agreement with the prediction by the classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [20,21]. However, there has been no systematic study so far on the transport behavior of nHAP, especially HA-modified nHAP in saturated packed column. Meanwhile, it is worth noting that in the presence of NOM and Ca^{2+} (e.g., groundwater environment), enhanced aggregation is observed due to the bridging of the nanoparticles by the microgels formed by the Ca-mediated bridging of NOM [22–24]. Therefore, it is crucial to investigate the impact of the divalent Ca^{2+} cation on the transport behavior of HA-modified nHAP colloidal particles in saturated packed columns.

In China, nHAP has been widely used as an ideal candidate for remediation of soils contaminated by heavy metals such as Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} [5]. Contaminants such as Cu ions are typically present in contaminated soil pore water solutions and groundwater environments in their dissolved state. The presence of dissolved Cu^{2+} ions in bulk solution can substantially change the electrochemical properties of colloidal particles having a significant influence on particle transport and deposition in porous media [25,26]. A more realistic investigation therefore entails observing the transport behavior of HA-modified nHAP in the presence of dissolved Cu^{2+} ions. This will be more closely minic conditions in natural soil and groundwater environments and thus allow for a more accurate simulation of their fate and transport in these systems.

In this work, a series of one-dimensional (1D) column experiments were conducted to assess the transport behavior of HA-modified nHAP in porous media. Experiments were conducted to investigate the effects of Cu concentration, IS, and IC on the transport behavior of HA-modified nHAP in saturated packed column.

2. Materials and methods

2.1. Porous media

Quartz sand obtained from Sinopharm Chemical Reagent Co., Ltd., China, was used as porous media. 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 sands were sonicated (KQ-300VDE sonicator, 100 W, 45 kHz, Shanghai, China) in 0.01 M NaOH solution for 30 min at room temperature, rinsed with deionized water, and then sonicated again for an additional 30 min in 0.01 M HCl solution before a final thorough rinsing with deionized water. The sands were then dried in an oven at 105 °C.

2.2. Characterization of nHAP

nHAP used in this study (purity > 99.99%) was purchased from Aipurui Nanomaterial Company (Nanjing, China). The nHAP was characterized by a variety of techniques. Powder X-ray diffraction (XRD) patterns were taken on a diffractometer (Shimadzu XRD-6000, Japan) with a Cu Kα radiation (40 kV, 30 mA). The scanning range (2θ) was from 10 to 80° at a speed of $5^\circ\ \mathrm{min}^{-1}$. The surface morphological features of the nHAP were observed using a Scanning Electron Microscope (LEO-1530 SEM, Germany). Crystal size and shape were studied by Transmission Electron Microscopy (JEM-2100 TEM, Japan), and the sample was prepared by placing a droplet of the colloidal suspension (200 $\mathrm{mg\ L^{-1}}$) on a Cu mesh TEM grid and left to air drying. The specific surface area of the nHAP was measured by nitrogen adsorption–desorption isotherms using the Brunauer–Emmett–Teller (BET) method (Micrometrics Accusorb 2100E, USA). The sample was degassed under vacuum at room temperature before measurement. The contents of Ca^{2+} and PO_4^{3-} in the nHAP were determined by Atomic Absorption Spectrometry (AAS, Hitachi Z-2000, Japan) and a molybdenum blue method [27], respectively. In order to eliminate the interference of PO_4^{3-} in measuring Ca^{2+}, masking agent (strontium chloride) was added in the test solution.

2.3. Adsorption isotherm of Cu on nHAP in the absence and presence of HA

Adsorption isotherms of Cu on nHAP in the absence and presence of HA were obtained by adding 2.5×10^{-2} g of nHAP to 5.0 mL of different concentrations of $Cu(NO_3)_2$ solution (analytical reagent) ranging from 0 to 5.0 mM in centrifuge tubes. Then, 20 mL ultrapure water (18.2 MΩ, Millipore, Inc., USA) containing 0 or 12.5 $\mathrm{mg\ L^{-1}}$ HA (Sigma Aldrich, Germany) in different sets was added, and the final volume was 25 mL. Therefore, the suspended Cu concentrations were 0, 1.0×10^{-2}, 2.0×10^{-2}, 0.10, 0.20, 0.50, 0.75, and 1.0 mM, respectively, and the concentrations of HA were 0 or 10 $\mathrm{mg\ L^{-1}}$ HA in different sets. The pH of the solutions was adjusted to 6.0 by adding 1.0×10^{-2} M HCl or NaOH solution. The experiments were conducted in triplicate.

Samples were continuously shaken for 24 h at 20 °C on a reciprocating shaker, centrifugated at 170,000*g* for 1 h (Optima TML-80XP Ultracentrifuge, Beckman), and then filtered through a 0.22 μm membrane filter. The Cu concentration in the filtrate was determined by AAS. The amount of Cu adsorbed onto the nHAP was calculated from the difference in concentrations between the initial and equilibrium solutions.

2.4. Preparation of nHAP colloidal suspensions

To test the effect of Cu concentration on the transport behavior of nHAP, a series of nHAP colloidal suspensions at varying initial Cu concentrations were prepared. The procedures are described below. First, 5.0×10^{-2} g of nHAP and 25 mL of 100 $\mathrm{mg\ L^{-1}}$ HA solution were added to a 250 mL volumetric flask, shaken vigorously for 1 min to disperse the nHAP. Then, 25 mL of different concentrations of Cu solution (1.0×10^{-2}–13 mM) and 200 mL ultrapure water were added. The final volume was 250 mL, and the concentrations of nHAP and HA were 200 and 10 $\mathrm{mg\ L^{-1}}$, respectively. The initial suspension Cu concentrations were 1.0×10^{-3}, 1.0×10^{-2}, 5.0×10^{-2}, 0.10, 0.50, and 1.3 mM. The colloidal suspension was sonicated (100 W, 45 kHz) for 30 min at room temperature. Prior to use, the suspension was stirred for 1 min to ensure a homogeneous suspension.

To determine the effects of IS and IC on the transport behavior of nHAP, experiments were conducted over a range of ISs (1.0, 10, 50, and 100 mM of KCl) and ICs (0.10, 0.30, 0.50, and 1.0 mM of $CaCl_2$). Here, the monovalent K^+ and divalent Ca^{2+} cations are selected in the experiments as these cations are abundant and omnipresent in the groundwater environments.