Blocking effect of colloids on arsenate adsorption during co-transport through saturated sand columns[☆]

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ABSTRACT

Transport of environmental pollutants through porous media is influenced by colloids. Co-transport of As(V) and soil colloids at different pH were systematically investigated by monitoring breakthrough curves (BTCs) in saturated sand columns. A solute transport model was applied to characterize transport and retention sites of As(V) in saturated sand in the presence of soil colloids. A colloid transport model and the DLVO theory were used to reveal the mechanism and hypothesis of soil colloid-promoted As(V) transport in the columns. Results showed that rapid transport of soil colloids, regulated by pH and ionic strength, promoted As(V) transport by blocking As(V) adsorption onto sand, although soil colloids had low adsorption for As(V). The promoted transport was more significant at higher concentrations of soil colloids (between 25 mg L^{-1} and 150 mg L^{-1}) due to greater blocking effect on As(V) adsorption onto the sand surfaces. The blocking effect of colloids was explained by the decreases in both instantaneous (equilibrium) As adsorption and first-order kinetic As adsorption on the sand surface sites. The discovery of this blocking effect improves our understanding of colloid-promoted As transport in saturated porous media, which provides new insights into role of colloids, especially colloids with low As adsorption capacity, in As transport and mobilization in soil-groundwater systems.

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1. Introduction

Colloidal particles are found in virtually all natural waters, including surface waters, soil pore waters, and groundwater systems (Bauer and Blodau, 2009; Kretzschmar and Schafer, 2005). Previous studies have indicated that the transport of pollutants (e.g., heavy metals, radioactive pollutants, and organic matter) through subsurface environments is facilitated by colloids (Denaix et al., 2001; Hammes et al., 2013; Honeyman, 1999; Kersting et al., 1999; Pedrot et al., 2008; Roy and Dzombak, 1997; Wang et al., 2011a; Yin et al., 2010; Zhang et al., 2005). The generally accepted mechanism of colloid-facilitated pollutant transport was that the colloid acts as a carrier to adsorb the pollutant and thus promote pollutant transport (Kanti Sen and Khilar, 2006).

To investigate the fate of colloid-associated pollutants, various three-phase transport models (Simunek et al., 2006), including the nonreactive colloids with the solid phase model, the first-order kinetic attachment of colloids model, the irreversible nonlinear kinetic attachment of colloids model, and the Langmuir kinetics attachment of colloids model, have been developed to delineate the pollutant transport in the presence of colloids (Grolimund and Borkovec, 2005; Grolimund et al., 1996; Saiers, 2002; Saiers and Hornberger, 1996; Simunek et al., 2006; Zou and Zheng, 2013). A model, only considering the colloid as a carrier, simulated kaolinite colloid-facilitated ^{137}Cs transport, but calculated data greatly deviated from the observed data obtained in experiments (Saiers and Hornberger, 1996). The adsorption of ^{137}Cs on kaolinite colloids is low, but the colloids greatly facilitate ^{137}Cs transport in the initial stage of breakthrough (Saiers and Hornberger, 1996). Unfortunately, little attention has been paid to this issue. Since most of

studies used colloids with a high adsorption capacity for pollutants during experiments (Grolimund and Borkovec, 2005; Grolimund et al., 1996; Saiers, 2002; Wang et al., 2011a, 2014), colloids mainly acted as carriers to facilitate the pollutant transport. Among them, ferruginous colloids (e.g., ferrihydrite colloids, Fe(III)-hydroxysulfates colloids, and Fe-NOM colloids) with a high adsorption capacity have been utilized to investigate facilitated As transport (Fritzsche et al., 2011; Guo et al., 2011; Neubauer et al., 2013; Slowey et al., 2007). Few similar phenomena were observed.

As the most common colloids in environment, soil colloids are composed of mineral colloids (phyllosilicate minerals containing Fe and Al oxides and amorphous minerals), organic colloids, and organo-mineral complexes colloids (Kretzschmar and Schafer, 2005). Similar to ^{137}Cs adsorbed onto kaolinite colloids, As adsorption onto soil colloids is relatively lower due to the limited effective adsorption sites of the colloid compared with those of the ferruginous colloids (Dousova et al., 2012). However, it is still unknown how soil colloid facilitate As transport.

Both soil colloid and As transport, especially As(V), in porous media are pH-dependent. Iron(III) (hydr)oxides, the main As-bearing minerals in porous media and soil colloid, are predominantly positively charged at pH 3.0—7.0 and negatively charged at pH 8.0—10.0 (Guo et al., 2014). Because As(V) is predominantly present as oxyanions ($H_2AsO_4^-$ and $HAsO_4^{2-}$) under pH > 4.0, the increase in pH to >8.2 drastically decreases As(V) adsorption onto Fe(III) (hydr)oxides (Qiao et al., 2012) due to the electrostatic repulsion, and thus promote As(V) transport in porous media and As(V) desorption from soil colloid. Therefore, soil colloid-associated As(V) transport would be dependent on pH. The variation of charge led to change of zeta potential. Negative zeta potentials of soil colloid and sand decrease with decreasing pH. Therefore, low pH promotes colloid deposition, which attributes to the decrease in repulsive interaction energies between colloids and grain surfaces (Wan and Tokunaga, 2002). In contrast, high pH enhances colloid transport due to the increased repulsive forces (Ryan and Elimelech, 1996).

The purpose of this study is to systematically investigate co-transport of soil colloids and As(V) at different pH in saturated sand columns. The effect of soil colloids and their concentrations on As(V) transport at different pH was assessed by monitoring breakthrough curves (BTCs). In addition, a solute transport model (Cameron and Klute, 1977; Selim et al., 1976) was used to simulate As(V) transport and evaluate retention sites of sand, and As(V) transport mechanisms in the presence of soil colloids were revealed with colloid transport model (Bradford et al., 2003) and DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948).

2. Materials and methods

2.1. Soil colloid suspension

The soil sample was collected from broad-leaved forest land in the Olympic Forest Park, Beijing, China. The sample was dried at room temperature (20 ± 5 °C), ground and sieved through a 0.074 mm nylon sieve to remove large particles. Soil colloid suspensions were prepared by adding 2.5 g of soil sample to 500 mL of Milli-Q water, homogenized by stirring, and sonicated for 60 min. After the solution settled for 24 h, the suspension was recovered by siphoning and further filtered through 1.2 μm membrane filter to remove the large suspended matter. Concentrations of soil colloid suspensions were determined by measuring the extinction at 420 nm with a spectrophotometer (UV5100B, METASH), based on the linear calibration curves between absorbencies and standards (Roy and Dzombak, 1997; Saiers and Hornberger, 1996; Shani et al.,

2008). Analytical methods for soil colloidal chemistry can be found in the Supplementary Material (S1).

The particle size distribution and zeta potential of the soil colloids were measured using a dynamic light scattering analyzer (Zetasizer Nano ZS, Malvern Instruments). The soil colloids were captured on 0.1 μm membrane filter by underpressure filtration to make the soil colloids flat. The contact angles (θ) of diiodomethane with known surface tension parameters on the soil colloids flat were measured using a drop shape analyzer (DSA 100, Kruss). Concentrations of dissolved cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, and Al^{3+}) and anions (Cl^-, F^-, NO_3^-, and SO_4^{2-}) in the filtrates of soil colloid suspensions were measured by inductively coupled plasma optical emission spectrometry (Optima 5300DV, Perkin-Elmer) and ion chromatography (ICS-900, Dionex Thermo Fisher), respectively. The morphological analysis of the soil colloid was achieved using scanning electron microscopy (SEM) using a Zeiss SUPRA 55 microscope (at 5 kV) and energy dispersive spectroscopy (EDS) (Zeiss SUPRA 55 SAPPHIRE, model) (Supplementary Material S1).

The particle size distribution of soil colloids used in this study at pH between 5.0 and 9.8 was 91.3—825.0 nm, with the fraction <100 nm less than 0.4%. In neutral and alkaline conditions, the size distribution and concentration of soil colloids were stable within 24 h (Supplementary Material S2).

Batch experiments were carried out to study As(V) adsorption onto soil colloids at different pH by reacting 25 mL of As(V) solutions (0.2—5 mg L^{-1} As) in 50 mL polypropylene shaking flasks with 250 mg L^{-1} of soil colloid suspensions. Stock solution (500 mg L^{-1} As(V)) was prepared from $Na_2HAsO_4 \cdot 7H_2O$ (Sigma-Aldrich), in Milli-Q water. The initial pH was adjusted to 5.0, 7.0, and 9.0 using 0.1 M HCl and 0.1 M NaOH. The flasks were placed in a shaking incubator that was held at 25 °C and shaken at 180 rpm for 24 h. The mixture was then centrifuged at 2000 g-force for 10 min, filtered through a 0.1 μm membrane filter, acidified with 1 M HNO_3 to pH < 2.0, and analyzed for As concentration within 24 h. The isotherm experiments were performed in triplicate. The data were used to evaluate adsorption isotherms according to Langmuir and the Freundlich isotherms (Supplementary Material S3).

2.2. Column experiments on co-transport of As(V) and soil colloid

Column experiments were conducted with glass chromatographic columns with a length of 20 cm and an inner diameter of 2.6 cm. The natural aquifer sand was used to simulate the groundwater environment. The sand was collected from an aquifer at a depth of 30 m below the land surface (the water table was approximately 25 m below the land surface) at the Astronomy and Earth Sciences Park of the Chinese Academy of Sciences, Chaoyang District, Beijing, China (40.00° N, 116.38° E), located in the middle of the Yongding River alluvial fan (Ma et al., 2015a). The column was wet-packed in Milli-Q water with a fixed amount of sand with grain sizes between 21 and 212 μm (with an average of 70 μm). A 38 μm fabric screen and 2 cm glass bead were placed at each end of the columns. The porosity and bulk density of the packed sand were 0.39 cm^3 cm^{-3} and 1.59 g cm^{-3}, respectively. After packing, the columns were pre-conditioned with around 50 pore volumes (PVs) of 0.001 mol L^{-1} HCl solution (pH ~ 3) using a peristaltic pump (BT-100 1F, Longer) in the up-flow mode.

In neutral and alkaline conditions (pH 7.2, 8.6, and 9.8), 25 PVs (~15 h) of 200 μg L^{-1} As(V) solutions with different concentrations of soil colloids suspensions (0, 25, 100, and 150 mg L^{-1}) were injected into the columns, followed by elution with 25 PVs of Milli-Q water with the same pH as the As(V) solution. At pH 5.0, 40 PVs (~24 h) of As(V) solution and 40 PVs of Milli-Q water were used for As(V) adsorption and elution, respectively. At pH 9.8, As(V) solution mixed with filtrated soil colloid suspension with 0.1 μm membrane