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 ¹³⁷Cs transport, but calculated data greatly deviated from the observed data obtained in experiments (Saiers and Hornberger, 1996). The adsorption of ¹³⁷Cs on kaolinite colloids is low, but the colloids greatly facilitate ¹³⁷Cs transport in the initial stage of breakthrough (Saiers and Hornberger, 1996). Unfortunately, little attention has been paid to this issue. Since most of

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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 ($20 \pm 5^\circ\text{C}$), 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 SAPHIRE, 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 ($0.2\text{--}5\text{ mg L}^{-1}$ 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 $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (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 $0.39\text{ cm}^3\text{ cm}^{-3}$ 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 $200\text{ }\mu\text{g L}^{-1}$ 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

was used as influent to exclude effects of soil colloid in a control experiment. To avoid As(V) adsorption on soil colloids outside the columns, a union tee was installed to mix them close to the inlet. All column experiments were at a constant Darcy velocity of $0.151 \text{ cm min}^{-1}$.

Concentrations of dissolved As(V) (C_{d-As}), total As(V) (C_{As}), soil colloid ($C_{colloid}$) and pH in effluent were measured for each 1–5 PVs. An aliquot was filtered through a $0.1 \mu\text{m}$ membrane filter to determine C_{d-As} , while an aliquot (4 ml) without filtration was mixed in 1 ml 0.5 M H_3PO_4 solution to determine C_{As} . Arsenic concentrations were analyzed by atomic fluorescence spectrometry (AFS-9800, KCHG). Concentrations of soil colloids ($C_{colloid}$) in the effluent were measured by spectrophotometer as mentioned above. The solution pH was monitored by a pH/ORP meter (S400 SevenExcellence, METTLER TOLEDO). Concentrations of dissolved cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and Al^{3+}) and anions (Cl^- , F^- , NO_3^- , and SO_4^{2-}) were measured to calculate ionic strength. Arsenic species in the effluent were determined by high performance liquid chromatography hydride generation atomic fluorescence spectrophotometer (PSA-10.825, PS Analytical). The speciation results showed that As(V) was not reduced during the experiments (the data was not shown).

Conservative tracer (Br^-) was used to check hydraulic characteristics of the columns. During column experiments, Br^- solution ($500 \mu\text{g L}^{-1}$) was introduced into the column as the same manner as the co-transport experiments. Effluent Br^- concentration was determined using an ion chromatography (ICS-900, Dionex Thermo Fisher). All column experiments were conducted in duplicate.

2.3. Mathematical models

Arsenic(V) adsorption onto soil colloids is ignored due to low adsorption (Supplementary Material S3). A chemical non-equilibrium model was used to simulate the As(V) transport and retention in the columns. Kinetic adsorption sites, including instantaneous equilibrium adsorption sites (Site-1_{As} , the sites are always at equilibrium) and first-order kinetic adsorption sites (Site-2_{As}), were considered (Cameron and Klute, 1977; Selim et al., 1976). S_1 and S_2 are the adsorbed As(V) contents in sand of Site-1_{As} and Site-2_{As} , respectively. In Site-1_{As} , the fraction of instantaneous adsorption sites (F) and linear adsorption coefficient (K_d) are used to account for As(V) instantaneous adsorption on the sand surfaces. In Site-2_{As} , the first-order rate coefficient for non-equilibrium adsorption (α) and the first-order decay coefficients for degradation in the solid phase (μ_s) are taken into account to calculate the time-dependent adsorption. The solute transport model is outlined in details in the Supplementary Material (S4).

Transport and retention of soil colloids in the columns were simulated using a one-dimensional model of the particle transport using attachment/detachment, chemical nonequilibrium with two-site kinetic retention (Bradford et al., 2003). The first kinetic $\text{Site-1}_{colloid}$, time-dependent retention, assumes reversible retention using first-order retention (k_{1a}) and detachment (k_{1d}) coefficients, and a Langmuir approach blocking function (Adamczyk et al., 1994; Wang et al., 2012) to account for maximum soil colloid content on $\text{Site-1}_{colloid}$ of sand (S_{max1}). The second kinetic $\text{Site-2}_{colloid}$, depth-dependent retention, assumes irreversible retention using a first-order retention coefficient (k_{2a}) and a depth-dependent blocking function (Bradford et al., 2003; Wang et al., 2012). s_1 and s_2 are the retained colloid contents in column sand associated with $\text{Site-1}_{colloid}$ and $\text{Site-2}_{colloid}$, respectively. Details on the colloid transport model and operative equations are shown in Supplementary Material (S5).

The interactions between soil colloids and the sand surfaces were elucidated on the basis of the Derjaguin-Landau-Verwey-

Overbeek (DLVO) theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948), which is the basis for understanding colloid transport and has a considerable amount of experimental support (Shani et al., 2008; Shen et al., 2015). A series of data (e.g., zeta potential, the radius, ionic strength, and contact angle) were used to calculate DLVO theory to elucidate the mechanisms of soil colloid transport. Details on DLVO theory and operative equations are given in the Supplementary Material (S6).

3. Results and discussion

3.1. Effect of pH on soil colloid-As(V) co-transport

BTCs for As(V) in Milli-Q water and As(V) with soil colloids in the saturated sand columns at different pH are shown in Fig. 1. In this study, As(V) transport increased with increasing pH from 5.0 to 7.2 (Fig. 1a and b), showing that high pH was conducive to As(V) transport in porous media (Charlet et al., 2011; Guo et al., 2014). Different pH levels near the column inlet were close to influent pH levels. This caused different As(V) transport, although pH levels in the effluents were slightly different (Supplementary Material S7). An inconspicuous increase in As(V) transport was observed when pH increased from 7.2 to 9.8 (Fig. 1b, c, and d). This can be explained by the little difference in As(V) adsorption on sand at these pH levels (between 7.2 and 9.8) (Ma et al., 2015a). The breakthrough plateaus of As(V) (Fig. 1a, b, and c) and As(V) recovery in the effluent (Table 1) with the presence of soil colloids were roughly identical to those in Milli-Q water at pH between 5.0 and 8.6, showing that the effect of soil colloids on As(V) transport was not obvious at these pH levels (between 5.0 and 8.6). In addition, As(V) concentration in the effluent greatly increased immediately after the influent was switched from As(V)-soil colloid solution to Milli-Q water at 42.5 PVs for pH 5.0 (Fig. 1a) and at 26 PVs for pH 7.2 and 8.6 (Fig. 1b and c), which results from an abrupt increase in the effluent pH due to lack of buffer ability of Milli-Q water relative to soil colloid suspensions (Supplementary Material S7) (Ma et al., 2015a).

However, soil colloids obviously increased As(V) transport at pH 9.8 (Fig. 1d). Arsenic(V) recovery in the effluent increased in the presence of soil colloids at the time of influent shift (from 52.9% to 66.8%) (Table 1). In the first 10 PVs, soil colloid-promoted As(V) transport (C_{As}/C_{As0}) and As(V) recovery in the effluent increased by more than 0.5 (50% As(V) co-transport with soil colloids) and 20% (from 20.7% to 42.4%) (Table 1), respectively, relative to As(V) transport in Milli-Q water. The evident colloid-promoted transport was unlikely due to the weak As(V) adsorption ($<3.7\%$) onto soil colloids (Supplementary Material S3), which was also supported by the fact that dissolved As concentration (C_{d-As}) was identical to total As (C_{As}) in the effluents (Supplementary Material S8). In the control experiment, As(V) transport in filtrate of soil colloid suspension was identical to that in Milli-Q water at pH 9.8. Therefore molecules and dissolved ions contributed little to promoting As(V) transport (Supplementary Material S9).

3.2. Effect of soil colloid concentration on As(V) transport

Forward breakthrough of As(V) was followed by slope side of plateau region with soil colloid concentrations of $25\text{--}150 \text{ mg L}^{-1}$, showing rapid transport relative to As(V) transport in the absence of soil colloids (Fig. 2a). The height of those plateaus was independent of soil colloid concentrations, which was different from other observations, showing the increase in plateau height of facilitated hydroxyatrazine transport with increasing concentration of clay colloid (Wang et al., 2014). However, the As(V) breakthrough time decreased with the increase in concentrations of soil colloids.

Fig. 1. Breakthrough curves of As(V) (initial concentration of $200 \mu\text{g L}^{-1}$) with soil colloids (initial concentration of 100 mg L^{-1}) and in Milli-Q water at influent pH 5.0 (a), 7.2 (b), 8.6 (c), and 9.8 (d). Symbols show observed data and solid lines show simulation fitting. Error bars represent the standard deviation of two replicates.

Table 1

Fitted parameters of As(V) transport in columns to the two-site sorption model (chemical nonequilibrium).

Influent	As(V) recovery-1 ^a (%)	As(V) recovery-2 ^b (%)	F ^c	K _d ^d (cm ³ ·g ⁻¹)	R ^e	$\mu_s^f \times 10^4$ (min ⁻¹ × 10 ⁴)	$\alpha^g \times 10^3$ (min ⁻¹ × 10 ³)	r ^{2h}
pH 5 in Milli-Q water	6.1 ± 0.8	39.4 ± 2.0	1.8E-01 ± 1.0E-02	1.8 ± 0.05	2.4 ± 0.12	1.9 ± 0.46	1.5 ± 0.36	0.93
pH 5 with 100 mgL ⁻¹ soil colloids	4.1 ± 0.6	40.1 ± 1.0	3.6E-01 ± 1.3E-01	2.0 ± 0.6	4.0 ± 0.17	0.47 ± 0.35	1.2 ± 0.72	0.98
pH 7.2 in Milli-Q water	18.6 ± 1.4	48.3 ± 1.6	1.9E-01 ± 2.1E-03	0.75 ± 0.04	1.7 ± 0.04	2.5 ± 2.2	2.7 ± 0.50	0.95
pH 7.2 with 100 mgL ⁻¹ soil colloids	14.3 ± 1.8	45.7 ± 1.3	4.3E-01 ± 7.4E-03	0.72 ± 0.15	2.4 ± 0.27	2.3 ± 2.5	3.3 ± 1.3	0.98
pH 8.6 in Milli-Q water	15.6 ± 0.4	47.6 ± 0.9	2.6E-01 ± 8.5E-04	0.90 ± 0.25	2.0 ± 0.30	2.8 ± 2.6	1.9 ± 1.2	0.96
pH 8.6 with 100 mgL ⁻¹ soil colloids	15.0 ± 1.2	46.6 ± 1.9	4.3E-01 ± 1.1E-02	0.56 ± 0.01	2.1 ± 0.00	6.1 ± 2.4	5.0 ± 0.74	0.99
pH 9.8 in Milli-Q water	20.7 ± 4.8	52.9 ± 2.7	2.1E-01 ± 4.6E-02	0.57 ± 0.11	1.5 ± 0.22	4.0 ± 0.98	3.4 ± 0.36	0.94
pH 9.8 with 25 mgL ⁻¹ soil colloids	42.5 ± 5.9	63.3 ± 0.8	1.8E-06 ± 1.1E-06	0.27 ± 0.05	1.0 ± 0.00	13 ± 2.9	7.0 ± 1.9	0.97
pH 9.8 with 100 mgL ⁻¹ soil colloids	47.7 ± 2.9	66.8 ± 1.9	8.0E-07 ± 5.8E-07	0.23 ± 0.04	1.0 ± 0.00	15 ± 6.6	6.1 ± 3.2	0.98
pH 9.8 with 150 mgL ⁻¹ soil colloids	52.9 ± 0.1	69.4 ± 0.3	6.7E-06 ± 7.3E-06	0.24 ± 0.09	1.0 ± 0.00	15 ± 6.0	4.4 ± 3.0	0.98

^a As(V) recovery in the effluent at 10 PV.

^b As(V) recovery in the effluent when the influent was switched from As(V) (-soil colloid) solutions to Milli-Q water.

^c The fraction of instantaneous adsorption sites was expressed in scientific notation due to large difference of orders of magnitude.

^d Linear adsorption coefficient.

^e The retardation factor was calculated as $R = 1 + F K_d \rho/\theta$.

^f The first-order decay coefficients for degradation in the solid phase.

^g The first-order rate coefficient for non-equilibrium adsorption.

^h Squared Person's correlation coefficient.

This indicates that colloid-promoted transport of As(V) is more evident with high soil colloid concentrations than with low concentrations. In comparison with low concentrations (25 and 100 mg L^{-1}), soil colloid at concentration of 150 mg L^{-1} increased As(V) transport (C_{As}/C_{As0}) by more than 0.2 and As(V) recovery in the effluent at 10 PV by 5–10%. Adsorption on soil colloids was not enough to account for this promoted transport due to the limited adsorption of As(V) on the soil colloids (Supplementary Material S3). Our observed results were consistent with a study by [Saier](#)

and [Hornberger \(1996\)](#), who reported that kaolinite colloid facilitated ^{137}Cs transport through saturated sand columns with low ^{137}Cs adsorption.

3.3. Simulation of As(V) transport

[Saier and Hornberger \(1996\)](#) suggested that the three-phase model better reproduces the experimental data of kaolinite colloid-facilitated transport of ^{137}Cs than the two-phase model.

Fig. 2. Breakthrough curves (a) and retention profiles (b–d) for As(V) under initial soil colloid concentrations of 0, 25, 100, and 150 mg L⁻¹, at influent pH 9.8. The retention profiles are shown at 5 PVs (b), 10 PVs (c), and 20 PVs (d). S_{1n} and S_{2n} represent $(S_1/C_{As0})/\text{gr sand}$ and $(S_2/C_{As0})/\text{gr sand}$, respectively. Symbols show observed data and lines show simulation fitting. Error bars represent the standard deviation of two replicates.

However, there were clear inaccuracies of the model considering the colloid as a carrier. In this study, although As(V) adsorption on soil colloids were higher around 4–10 times than on sand (Ma et al., 2015a) and adsorbed-As(V) concentrations on soil colloids were higher than As concentrations of some As-contaminated soils (Ma et al., 2016), the adsorption was much less than on ferrous minerals (e.g., ferrihydrite, siderite, goethite, magnetite, and mixture of siderite and goethite) (Asta et al., 2009; Guo et al., 2010; Jessen et al., 2005; Liang and Zhao, 2014). Soil colloid suspensions with concentrations of 250 mg L⁻¹ only adsorbed 8.9%, 5.7%, and 3.7% As(V) from 200 µg L⁻¹ As(V) solution at pH 5.0, 7.0, and 9.0, respectively (Supplementary Material S3). Lower adsorption on soil colloids was expected to occur in porous sand column experiments with 25–150 mg L⁻¹ soil colloids, and 200 µg L⁻¹ As(V). Therefore, As(V) adsorption onto soil colloids was low and can be ignored.

Based on a two-phase chemical non-equilibrium model, the inverse routine was directly implemented in HYDRUS-1D 4.xx and used to estimate transport and reaction parameters using a Levenberg-Marquardt algorithm (Marquardt, 1963). The fitted curves are shown in Figs. 1 and 2, and Table 1 presents the fitted parameters of those observations. Prior to fitting the simulation, the breakthrough curves of conservative tracer (Br⁻) were used to estimate the longitudinal dispersivity, λ , using the CXTFIT code (STANMOD) (Supplementary Material S10) (Toride et al., 1999).

Abrupt increases in As(V) in Fig. 1a, b, and c at the time of influent shift were ignored during the simulation. The correlation coefficient ($r^2 > 0.93$) between the experimental and predicted data confirmed satisfactory fits (Figs. 1 and 2). The linear adsorption coefficient, K_d , decreased with the increase in pH, showing the

decrease in As(V) adsorption with increasing pH. The first-order rate coefficient for non-equilibrium adsorption, α , and the first-order decay coefficients for degradation in the solid phase, μ_s , varied from $1.2 \times 10^{-3} \text{ min}^{-1}$ to $7.0 \times 10^{-3} \text{ min}^{-1}$ and from $0.47 \times 10^{-4} \text{ min}^{-1}$ to $15 \times 10^{-4} \text{ min}^{-1}$, respectively (Table 1). Although the values of α and μ_s changed with experiment conditions, both were relatively low, indicating that As(V) adsorption onto Site-2_{As} and degradation from Site-2_{As} were slow and thus had limited effect on As(V) transport, especially at the initial stage.

Noticeably, the fraction of instantaneous adsorption sites, F , in the presence of soil colloids at pH 9.8 was much lower than those with or without soil colloids at pH 5.0, 7.2, and 8.6 (roughly 5 orders of magnitude) (Table 1). This indicates that trace amounts of As(V) would be instantaneously adsorbed onto Site-1_{As} in the presence of soil colloids at pH 9.8, while around 20–40% As(V) was adsorbed onto Site-1_{As} in other experimental conditions. The decreases in F values were comparable to the report by Jellali et al. (2010) who observed that the increase in the flow rate of ammonium solutions from 15 ml min⁻¹ to 45 ml min⁻¹ led to significant decreases in instantaneous adsorption. The present study was carried out at a constant flow rate, at pH 9.8 and concentrations of soil colloids between 25 and 150 mg L⁻¹. It indicates that soil colloid-promoted As(V) rapid transport was caused by the decrease in instantaneous adsorption onto Site-1_{As}. Because of very low F values, the retardation factor (R) was calculated as roughly equal to 1 (Table 1), showing non-retardant As(V) transport in the presence of soil colloids at pH 9.8 relative to other experiment conditions.

The retention profiles (RPs) for As(V) in the porous media were evaluated at different PVs from 5 to 20 at pH 9.8 (Fig. 2b, c, and d).

The RPs are plotted as initial As(V) concentration normalized-As(V) retention (As(V) retention in the sand columns, S_1 and S_2 , divided by the initial As(V) concentration, C_{As0}) per gram of dry sand as a function of distance from the column inlet. S_{1n} and S_{2n} represent $(S_1/C_{As0})/\text{gr sand}$ and $(S_2/C_{As0})/\text{gr sand}$, respectively. Arsenic(V) instantaneous adsorption (S_{1n}) was roughly equal to 0.1 at profiles with the absence of the soil colloids, which is much higher than that ($<10^{-4}$) of As(V) instantaneous adsorption (S_{1n}) in profiles for the soil colloid-treated experiments (Fig. 2b, c, and d). In comparison with S_{1n} , the first-order kinetic adsorption (S_{2n}) is higher in the presence of soil colloids, showing the predominant role of Site-2_{As} in As adsorption. At 5 PVs, more As(V) adsorption on Site-2_{As} (S_{2n}) was observed near the column outlet in the soil colloid-treated experiments than in the soil colloid-free experiments, while higher As(V) retention was found near the column inlet in the soil colloid-free experiments (Fig. 2b). Accordingly, high As(V) concentrations which were co-transported with soil colloids to column outlet were earlier than As(V) transport without the colloids. During transport, the increase in S_{2n} in the column with increasing pore volumes was observed in the soil colloid-free experiments, which is more apparent than the increase in S_{2n} in column during soil colloid-treated experiments (Fig. 2b, c, and d). At 10 PVs, As(V) adsorption (including S_1 and S_2) in the soil colloid-free column exceeded that in the soil colloid-treated columns. Therefore, the fast As(V) transport in the presence of the colloid was caused by low adsorption in the column, including the instantaneous adsorption and the first-order kinetic adsorption.

3.4. Transport of soil colloids

BTCs and RPs for soil colloids in the columns were evaluated at different pH levels between 5.0 and 9.8. Fig. 3 and Table 2 present the simulation results and fitted parameters, respectively. Overall, retention of soil colloid decreased with increasing pH (Fig. 3). Although the breakthrough plateaus were identical at pH 8.6 and 9.8 (Fig. 3c, d, e, and f), the kinetic model parameters and soil colloid recovery in the effluent (Table 2) were quite different at those two pH levels, showing the difference in soil colloid transport. The two-kinetic site model parameters k_{1a} , k_{2a} , and $S_{\max 1}$ decreased with increasing pH, while k_{1d} and k_{1d}/k_{1a} increased (Table 2). In alkaline conditions, especially at pH 9.8, the values of k_{1d}/k_{1a} were higher than 1 (Table 2), indicating that retention of soil colloids on time-dependent sites (Site-1_{colloid}) was low due to the stronger detachment interaction between soil colloids and sands than attachment (Sun et al., 2015a). In contrast, soil colloids were readily retained on the sand in acidic environments.

The RPs are plotted as initial soil colloid concentration-normalized soil colloid retention (soil colloid retention in the sand columns, S_{colloidr} , divided by the initial soil colloid concentration C_{colloid0}) per gram of dry sand as a function of distance from the column inlet. Due to the difficulty in distinguishing soil colloid from sand chipping, soil colloid retention in the sand columns was not measured in this study. However, the values of model fitting was employed to describe soil colloid retention in all columns (Sun et al., 2015b; Wang et al., 2012; Wang et al., 2013). The amount of retained soil colloids sharply decreased with increasing pH. The strained soil colloid was mostly retained near the column inlet. The normalized soil colloid retention decreased with increasing distance from the column inlet (Fig. 3g). The small pores caused soil colloids to be blocked near the column inlet, which resulted in dead-ends of collector pores and consequently restricted mobility of soil colloids in continuous pore networks (Bradford and Bettahar, 2006; Liang et al., 2013).

At pH 9.8, regardless of concentrations of soil colloids (25, 100, and 150 mg L⁻¹), the breakthrough plateaus were similar (Fig. 3d, e,

and f). However, the soil colloid retention decreased with decreasing concentrations of soil colloids (Fig. 3g). Accordingly, k_{2a} , the first-order retention coefficient on Site-2_{colloid}, showed the same trend (Table 2).

DLVO theory was used to calculate the interaction forces between the soil colloid and the sand, assuming plate-plate interactions (Feriancikova and Xu, 2012; Wu et al., 2013), in order to explain the mechanisms of soil colloid transport and retention in porous media. The DLVO energy interactions, the sum of van der Waals attraction and electric double layer repulsion between the soil colloid and the sand surface, were calculated. Results are shown in Fig. 4, and parameters used in calculation are listed in the Supplementary Material (S11). Under the pH of the experiments, the corresponding zeta potentials of the soil colloids (−15.7 to −21.6 mV) and sand (−23.1 to −40.8 mV) increased with decreasing pH (Supplementary Material S11), which could be explained by the compression of the electric double layer as a result of high H⁺ concentration (Ma et al., 2015b). However, the radius of the soil colloids (119.8–168.2 nm) increased with decreasing pH due to coagulation in acidic conditions.

Since the major ions (i.e., K⁺, Na⁺, Ca²⁺, Mg²⁺, Al³⁺, Cl[−], F[−], NO₃[−] and SO₄^{2−}) were dissolved at different pH, colloidal suspensions had the specific ionic strength (~4.5–7 mM) in column experiments (Table S11). Calculations showed that the magnitude of the primary energy barrier ranged from ~100 to ~300 kT (Fig. 4a), which increased with increasing pH and decreasing ionic strength with the opposite variation trend to k_{1a} , indicating that soil colloid transport readily increased with increasing pH and with decreasing ionic strength. At pH 5.0–8.6, soil colloid-sand interaction energy readily exceeded the primary energy barrier (~100–~150 kT) and thus soil colloids irreversibly deposited into the primary energy minimum. But, at pH 9.8, soil colloid was difficult to deposit into the primary energy minimum due to the high primary energy barrier (>250 kT). The retention of the soil colloids at pH 9.8 possibly occurred mainly through their entrapment within the secondary energy minimum (Feriancikova et al., 2013; Wang et al., 2011b), where the soil colloid is easily removed by kinetic energy of diffusing (Fig. 4b). Because of low ionic strength, the sand-colloid system with soil colloid of 25 mg L⁻¹ at pH 9.8 had a higher primary energy barrier and a shallower secondary energy minimum than those with soil colloid concentrations of 100 mg L⁻¹ and 150 mg L⁻¹ at pH 9.8. This indicated that the soil colloid with low concentrations at pH 9.8 was more readily transported in comparison with those with high concentrations. The trend extended the results of the soil colloid transport model.

3.5. Mechanism and hypothesis of soil colloid-promoted As(V) transport

Soil colloid-promoted As(V) transport was observed in porous media with low As(V) adsorption onto soil colloid. Less retained co-transport of As(V) and soil colloid occurred at pH 9.8, although it was retarded under other pH conditions, suggesting that a repulsion between sand and soil colloid was the basis of the phenomenon. The rapid transport of kaolinite colloids was reported in kaolinite colloid-facilitated ¹³⁷Cs transport (Saiers and Hornberger, 1996), which verified our viewpoint. Although As(V) transport at pH 8.6 was identical to that at pH 9.8 in the absence of soil colloids (Fig. 1c and d), the colloid-promoted transport was not observed in the presence of soil colloids at pH 8.6. However, evident colloid-promoted As(V) transport was found at pH 9.8, indicating that strong repulsion between sand and soil colloids could lead to soil colloid-promoted As(V) transport. During kaolinite colloid-facilitated ¹³⁷Cs transport, high ionic strength decreased repulsion for kaolinite colloids, and thus the level of facilitated ¹³⁷Cs transport

Fig. 3. Breakthrough curves (a–f) and retention profiles (g) for soil colloids at different influent pH and initial concentrations of soil colloids. Symbols show observed data and lines show simulation fitting. Error bars represent the standard deviation of two replicates.

Table 2
Fitted parameters of soil colloid transport in columns to the two-kinetic site model (particle transport using attachment/detachment, chemical nonequilibrium).

Influent	Soil colloid recovery ^a (%)	$k_{1a}^b \times 10^3 \text{ (min}^{-1}\text{)}$	$k_{1d}^c \times 10^3 \text{ (min}^{-1}\text{)}$	$k_{2a}^d \times 10^2 \text{ (min}^{-1}\text{)}$	k_{1d}/k_{1a}	$s_{\text{max}1}^e \times 10^{-6}$	r^{2f}
pH 5.0 with 100 mg L ⁻¹ soil colloids	13.0 ± 0.3	17 ± 0.73	1.4 ± 0.21	21 ± 2.3	0.084 ± 0.016	4.7 ± 4.9	0.91
pH 7.2 with 100 mg L ⁻¹ soil colloids	36.8 ± 1.5	6.4 ± 0.28	1.4 ± 0.13	8.8 ± 0.82	0.21 ± 0.011	2.5 ± 2.4	0.96
pH 8.6 with 100 mg L ⁻¹ soil colloids	79.2 ± 1.4	3.5 ± 0.14	5.7 ± 0.94	1.4 ± 0.36	1.6 ± 0.20	2.4 ± 3.3	0.98
pH 9.8 with 25 mg L ⁻¹ soil colloids	93.0 ± 0.6	1.9 ± 0.59	5.8 ± 1.1	0.39 ± 0.10	3.1 ± 0.41	2.8 ± 0.28	0.94
pH 9.8 with 100 mg L ⁻¹ soil colloids	87.4 ± 1.1	1.1 ± 0.24	2.4 ± 0.75	0.45 ± 0.23	2.2 ± 0.22	1.4 ± 0.04	0.94
pH 9.8 with 150 mg L ⁻¹ soil colloids	91.4 ± 0.1	0.93 ± 0.13	5.4 ± 1.3	0.59 ± 0.08	5.8 ± 0.57	1.7 ± 0.34	0.94

^a Soil colloid recovery in the effluent when the influent was switched from As(V)-soil colloid solutions to Milli-Q water.
^b The first-order retention coefficient on Site-1_{colloid}.
^c The first-order detachment coefficient on Site-1_{colloid}.
^d The first-order retention coefficient on Site-2_{colloid}.
^e Maximum solid phase concentration of soil colloids on Site-1_{colloid}.
^f Squared Person's correlation coefficient.

drastically decreased and was equivalent to adsorption-facilitated kaolinite colloid transport (Saier and Hornberger, 1999). Soil colloid transport was enhanced with decreasing soil colloid concentration due to low ionic strength, since the soil colloid was contributing to the ionic strength. However, promoted As(V) transport increased with increasing soil colloid concentration at pH 9.8, although a high ionic strength was associated with a high concentration of soil colloid. According to the DLVO theory (Feriancikova and Xu, 2012; Wu et al., 2013), when the colloids

approached the surface of porous media, the electric double layer repulsion would prevent colloids from landing on the surface of porous media at a certain pH (pH 9.8 in this study), and thus colloidal transport was active in porous media. Based on this investigation, the hypothesis was developed and shown in Fig. 5. Arsenic(V) transport was positively affected by rapid colloidal transport. At pH 9.8, during As(V) transport from solution to sand, the moving paths of As(V) were blocked by the rapid colloidal transport, where the mobile soil colloids readily collided with As(V)

Fig. 4. DLVO interaction energy between soil colloids and sands. The primary energy barriers for soil colloids and sand (a) and the secondary energy minimum for soil colloids and sand (b). The interaction energy was expressed in kJ, where k is the Boltzmann constant, and T is absolute temperature in Kelvin.

and retarded the As(V) arriving to the sand surface (Fig. 5). The collision should effectively change the transport direction of As(V). However, at pH 5.0, 7.2, and 8.6, soil colloid deposition caused As(V) and soil colloid to move in one direction toward sands, leading to the inefficient collision, whereas at pH 9.8, As(V) hardly crossed the “highway of soil colloid” to be adsorbed onto sand due to limited soil colloid deposition (Fig. 5). The phenomenon would be more significant with higher soil colloid concentrations. The blocking effect of soil colloid on As(V) retention onto sand decreased As(V) adsorption on both instantaneous and first-order kinetic sites, and therefore promoted As(V) transport in the porous media.

4. Conclusions

As the third phase except for stationary phase (consisting of subsurface solids) and the mobile aqueous phase (as the medium for the movement of dissolved chemical species), colloids can increase the apparent solubility of low-soluble pollutants and thus facilitate transport of those pollutants, which greatly improves the mobility of pollutants (Kretzschmar and Schafer, 2005). Our study extended this current theory, by showing that the presence of soil

colloids with low As(V) adsorption capacity accelerated As(V) transport in porous media. Results show that strong repulsion between porous media and soil colloids led to soil colloid-promoted As(V) transport by blocking As(V) adsorption onto porous media. They indicate that colloids can play an important role in facilitating solute transport, not only as a carrier in the course of solute transport but also as a barrier in the course of solute adsorption. The blocking effect of colloid should be ubiquitous in natural aqueous environments, with similar colloid concentrations to this study between 1 and 60 mg L⁻¹ in groundwater (Ronen et al., 1992; Ryan and Gschwend, 1990) and the strong steric repulsion of colloids at normal pH, such as montmorillonite colloid (Shen et al., 2015) and kaolinite colloid (Saiers and Hornberger, 1996). This finding provides a new insight into colloid-facilitated transport, especially for colloids with low adsorption capacity for pollutants, in complex soil and groundwater systems, such as surface water infiltration systems, and hyporheic zones with intensive interaction between surface water and groundwater. Future investigation will evaluate the effects of flow rate, geometry of colloid-systems, type of porous media, and type of colloid, especially inert microspheres to eliminate complicated interaction between soil colloids and

Fig. 5. Hypothetic diagram of blocking effect of soil colloid on As(V) adsorption onto sand during co-transport.

porous media, on colloid-promoted solute transport.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.03.020>.

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