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ABSTRACT

Vanadium, a hazardous pollutant, has been frequently detected in soil and groundwater, however, its transport behavior in porous media were not clearly understood. In this study, the effects of solution pH, ionic strength (IS) and the effect of clay mineral on the transport of vanadium in saturated porous media were investigated. Laboratory experiments using a series of columns packed with quartz sand were carried out to explore the retention and transport of vanadium with a range of ionic-strength (0.001–0.1 M) and pH (4–8) and two different types of clay minerals montmorillonite and kaolinite. Results of the breakthrough experiments showed that vanadium was highly mobile in the saturated porous media. The increase in pH rendered a higher transport of vanadium in saturated porous media. The study also indicated an easier transfer of vanadium with an increase in IS. Montmorillonite enhanced the mobility of vanadium in the column when compared to kaolinite. A mathematical model based on advection-dispersion equation coupled with equilibrium and kinetic reactions was used to describe the retention and transport of vanadium in the columns very well.

1. Introduction

Vanadium(V), a ubiquitous element in the natural environment,[1] has attracted much attention recently due to its potential environmental and health risks. Vanadium pollution may not immediately threaten ecosystems on a global scale but the deposition, accumulation and migration of high levels of vanadium in the range of 2–310 mg/kg, may cause serious environmental problems [1] due to its potential to leach to the groundwater contaminating drinking water supplies. With large-scale mining, smelting and processing of vanadium, vanadium are released into the environment. Other sources of vanadium release include oil refineries and power plants using vanadium rich fuel oil and coal.[2]

The distribution, fate and transport of vanadium are affected by several factors which include (a) the rusting process in the soil,[3] (b) oxidation state of vanadium [4] and (c) the presence of carbonates in soils.[4] Mandiwana and Panichev [5] concluded that the presence of atmospheric CO_2 and ammonia can enhance the leaching of vanadium from soils. In agricultural soils and mine tailings in the Panzhihua region, vanadium showed low mobility and leachability, but its mobility increased with alternating wet and dry conditions.[1] Other studies have indicated that the adsorption of vanadium was

also dependent on soil pH,[6] the presence of iron and manganese oxides [7] and soil texture.[8] Compared to clay and silt soils, sandy soil has lower sorption ability for vanadium due to the occurrence of ion-exchange sites [9] and low oxalate soluble Fe, Mn and Al concentrations.[3,8] Parent material is also another important factor affecting vanadium uptake and mobility.[8] Most of the previous studies on the distribution, mobility, and adsorption of vanadium in soils were based on batch experiments under optimized conditions of sufficient interaction time and contact. Only few studies examined the dynamics of vanadium deposition and transport in porous media under flow through conditions. Therefore, additional investigations are required to improve current understanding of how flow dynamics may affect the retention and transport of Vanadium in porous media.

The main factors controlling the transport of heavy metals in porous media can be classified as follows: mechanical factors such as molecular shape, flow rate, and influent concentration; and physicochemical factors such as ionic strength, pH, and porous media surface. These factors are interrelated. For example, the molecular shape is dependent on the solution pH and ionic strength.[10] Experimental breakthrough curve (BTC) study of four heavy metal ions (Pb^{2+}, Zn^{2+}, Mn^{2+} and

Ni^{2+}) revealed that Pb^{2+} has the highest retention rate and retardation factor at both pH 4.0 and pH 5.0.[11] Several studies have also shown that flow rate and solution ionic strength (IS) also have strong impact on the fate and transport of heavy metals in soils.[12,13]

Mobile soil colloids have been extensively studied in recent years because of their role in contaminant transport through soils and groundwater.[14] Colloid facilitated transport of heavy metals in soils has also been reported [15–17] and it has been recognized as one of the most important mechanisms governing the mobility of heavy metals in soils, and thus has attracted much attention.[18,19] Clay minerals, with relative high surface area, negative surface charge, and strong interaction with cations, have a strong ability to adsorb various chemical species particularly heavy metals.[15,20,21] Although colloidal clay minerals are known to affect the retention and transport of heavy metals in soils, there are still not many experimental studies focusing on colloid-facilitated vanadium transport in water-saturated porous media. Therefore, further investigations on the interaction between colloids and vanadium with the surrounding media should be carried out to strengthen the understanding of the interactions effect on the dynamic behavior of vanadium, colloids, and their complexes.

Based on the findings of previous studies, we hypothesized that solution pH, ionic strength, as well as the clay minerals are the key factors controlling vanadium transport in saturated porous media. To test the hypothesis, laboratory quartz sand column experiments were conducted to investigate the effect of solution ionic strength and pH on vanadium transport in saturated porous media. In addition, two common clay minerals, montmorillonite and kaolinite, were selected in this study to assess the importance of colloidal clay mineral in the retention and transport of vanadium in saturated porous media.

2. Materials and methods

2.1. Materials

Vanadium solution was prepared with deionized (DI) water at a concentration of 50 mg/L (ammonium metavanadate, NH_4VO_3; Chengdu Kelong Chemical Reagent Company). The colloidal kaolinite and montmorillonite (Shanghai Fengxian Fengcheng Chemical Reagent Company) were prepared according to the procedure of Sun et al. [22]. 10.0 g of colloid was suspended in 1 L DI water. The suspension was shaken vigorously, placed in an ultrasonic bath for 30 min, and then allowed to sit for 24 h. The fraction of colloid remaining in suspension after 24 h was siphoned into a second flask. The concentration of colloid in this suspension was determined gravimetrically before diluting an aliquot of the stock to proper colloid concentration. Quartz sand (Shaanxi Zhouzhi Counry Quartz Sand Company) sieved to a size range of 0.4–0.5 mm was used as the porous medium in

the column experiments. Prior the column packing, the sand was washed with 0.1 M NaOH solution for 12 h to remove surface metallic compounds and then washed with 0.1 M HCl solution for 12 h to remove organic impurities, followed by washing with deionized water until there was no impurities was detected, and sequentially dried in an oven at 105 °C for 3 h.

2.2. Column experiments

The quartz sand was wet-packed into a column measuring 3.0 cm in diameter and 15 cm in height.[23] To make a saturated porous media, a small amount of quartz sand was poured gently into 10 mL of DI water standing at the bottom of the column until the sand surface was 0.5–1 cm below the water level. A polypropylene stir-rod was used to stir the sand in the column. Sequentially, approximately 10 mL DI water was then added to the column. This procedure was repeated several times until the column was packed to a height of 15 cm. Approximately 146 g of sand was used to pack one column with a porosity of 0.42. The zeta potential was determined by measuring the electrophoretic mobility of colloidal quartz sand.[24] For colloidal sand, a mixture containing 50 g of clean quartz sand and 100 mL DI water was first ultrasonicated for 30 min. Then the aliquots of the quartz colloids were removed and filtered through a 0.45 μm filter and the filtrate was analyzed for electrophoretic mobility (U) with a ZetaPlus (Brookhaven Instrument Co). The Smoluchowski's formula was used to transfer electric mobility of the quartz sand into zeta potential ($\zeta = 4\pi\eta U/\varepsilon$, where η is the viscosity of the medium and ε is the dielectric constant).

The saturated column was leached with DI water for 2 h to remove impurities, followed by leaching with different working solutions. The column was then allowed to stand overnight to stabilize the pore water pH and ionic strength (IS). Cl^- was used as the tracer element of the breakthrough curve study in this experimental process. The column was first leached with potassium chloride (0.01 M) followed by DI water at a specific velocity of 0.14 cm/min. Samples at the column outlet was collected in glass vials every 10 mL with an automatic fraction collector. For each column, the experiments were conducted with different pH (4, 6, 8) and IS (0.1, 0.01, 0.001 M) conditions. The pH of leaching solution was adjusted with 0.5 M NaOH and HCl, the ionic strength (IS) was regulated with KCl. A peristaltic pump was used to control the upward flow at a constant specific velocity of 0.14 cm/min. Once the outflow was stabilized, the leaching experiment was then initiated by switching the inflow to vanadium solution. For all experiments, the inflow concentration of vanadium was 50 mg/L, which was within the range of their typical average soil vanadium concentrations.[1] In this study, the vanadium solution was firstly applied to the column,

then the experiments were operated into two sections: (1) the column was leached with DI water at various pH and IS conditions; (2) the column was leached with kaolinite and montmorillonite colloids at constant condition, respectively. Samples at the column outlet was collected in glass vials every 10 mL with an automatic fraction collector. In the leachate, kaolinite and montmorillonite colloid concentration was analyzed by UV/VIS at 350 nm and 243 nm, respectively, and vanadium was analyzed for by FAAS after acidification.

2.3. Modeling of vanadium transport in saturated porous media

One dimensional advection-dispersion equation coupled with reaction terms was used to simulate the transport of vanadium in water saturated quartz sand column. We presumed that the interaction between the vanadium and the sand grains in the column were affected by both reversible-equilibrium and irreversible-kinetic reaction. [25] The governing equation can be written as:

$$R\frac{\partial C_w}{\partial t} = D\frac{\partial^2 C_w}{\partial z^2} - v\frac{\partial C_w}{\partial z} - kC_w \tag{1}$$

where C_w is the concentration (vanadium) in pore water (mg L^{-1}); R is the retardation factor, which reflects the magnitude of equilibrium reactions in the quartz sand column; D is the dispersion coefficient (cm^2 min^{-1}); v is the flowrate of pore water (cm min^{-1}); and k is the irreversible, first-order kinetic reaction rate constant (min^{-1}).

The governing equation of the transport model numerically was treated as a zero initial concentration, a pulse-input boundary condition at the column inlet, and a zero-concentration-gradient boundary condition at the outlet. The Levenberg–Marquardt algorithm was used to estimate the value of the model parameters to minimize the sum-of-the-squared differences between model-calculated and measured breakthrough concentrations. The model was first applied to the chloride breakthrough data to estimate dispersion coefficient (D).

3. Results and discussion

3.1. Effects of pH on the transport of vanadium in water saturated quartz sand column

Compared to the chloride, the transport of vanadium in the porous media under different pH conditions was delayed (Figure 1). As pH increased, the normalized peak concentration (C/C_0) of vanadium accordingly was gradually enhanced from around 1.26, 1.35 to 1.42. When pH was increased from 4 to 8, the Zeta potential of colloidal sand suspension decreased from −28.5 mV, −30.9 mV to −45.1 mV (Table 1). The pH increase made the sand surface more negative, reduced the sorption of VO$_3^-$ on
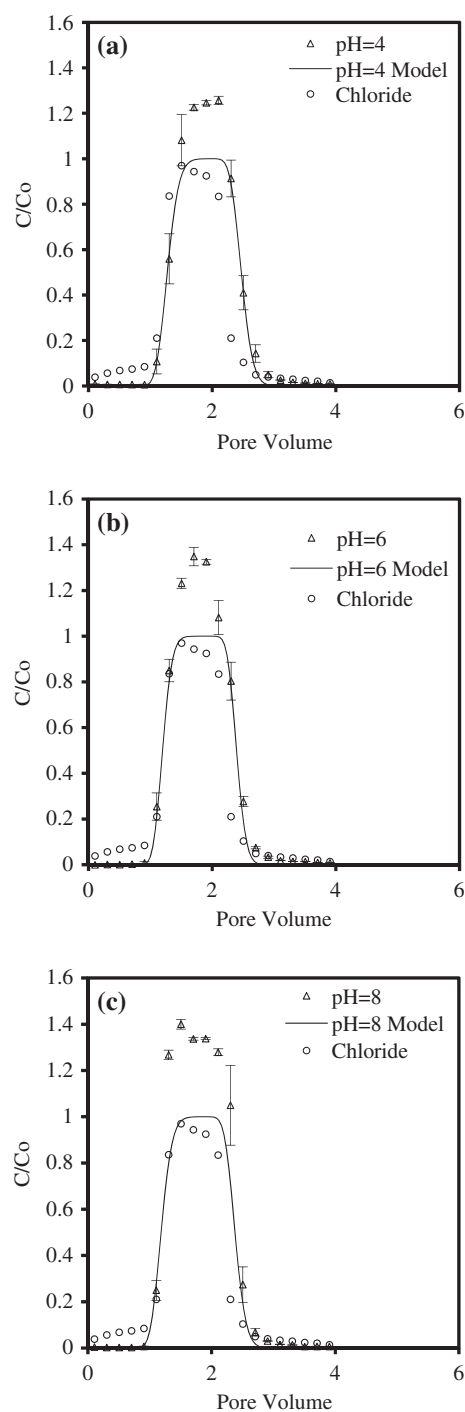

Figure 1. Effects of pH on the transport of vanadium in water saturated quartz sand columns.

the quartz sand. Model simulations matched with the vanadium breakthrough curve with R^2 of 0.9536, 0.9382, and 0.8723, respectively (Table 2).

3.2. Effects of IS on the transport of vanadium in water saturated quartz sand column

The transport of vanadium in the porous media showed some delay and displayed asymmetry (Figure 2). Solution IS 0.01 M showed less effect on vanadium transport in the quartz sand column. This was probably due to the fact that, under the experimental condition, electrostatic
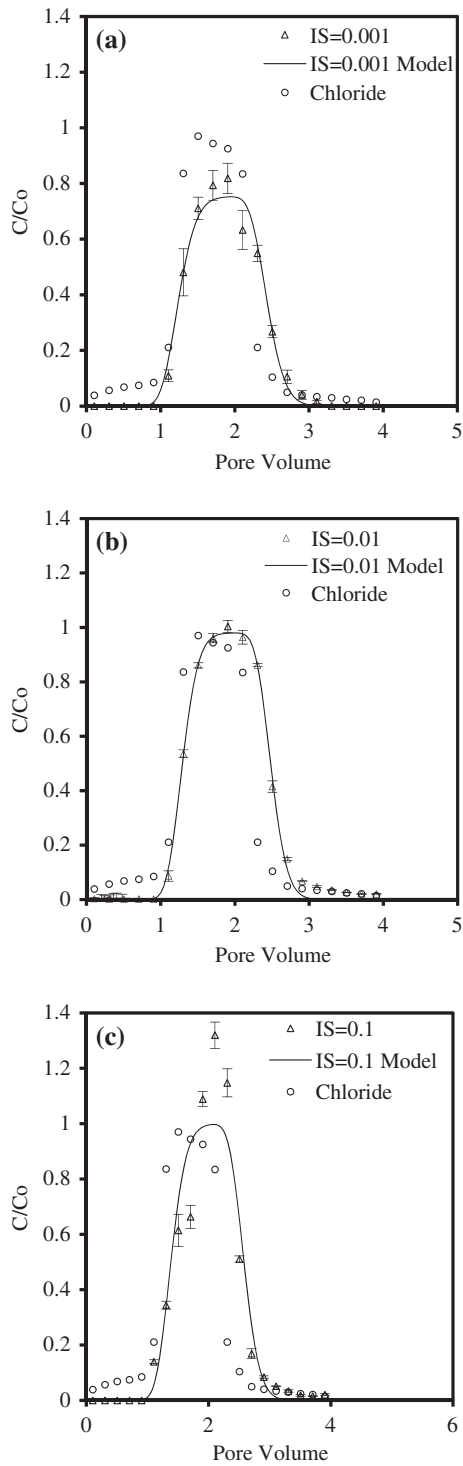
Figure 2. Effects of IS (a) IS = 0.001 M; (b) IS = 0.01 M; (c) IS = 0.1 M on the transport of vanadium in saturated quartz sand columns.
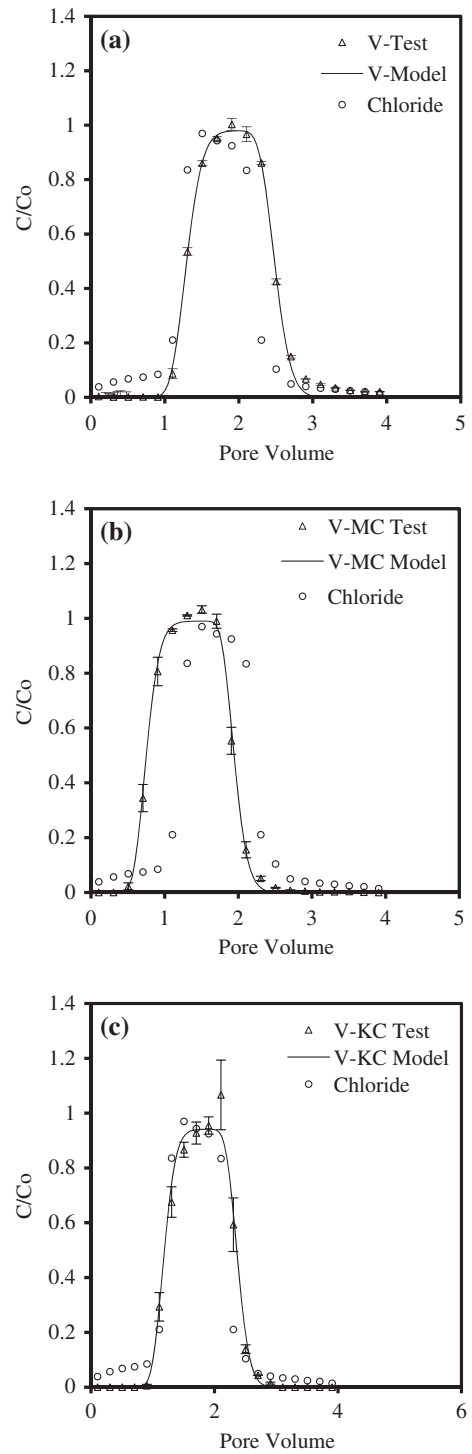
Figure 3. Effects of clay minerals (a, transport of vanadium; b, montmorillonite colloid; c, kaolinite colloid) on the transport of vanadium in saturated quartz sand columns.

Table 1. Zeta potential of sand colloidal suspensions as a function of solution pH and IS.

pH	4	6	8
IS/M	0.01	0.01	0.01
Zeta/mV	−28.5	−30.9	−45.1

interactions between the VO_3^- anion and the quartz sand were negligible, and thus there was no competition effect from the cations or anions in the electrolyte. When

the electrolyte concentration decreased to the 0.001 M, the normalized peak concentration (C/C_0) of vanadium were accordingly reduced, which indicated that the

Table 2. Best-fitting parameters of vanadium in water saturated quartz sand column perturbed with pH.

Factor	D (cm^2 min^{-1})	R	K (min^{-1})	R^2
Chloride	0.02549	–	–	–
pH = 4	–	21.81	0.00000015	0.9536
pH = 6	–	26.76	0.0000002218	0.9382
pH = 8	–	19.44	0.0000032	0.8723

Table 3. Best-fitting parameters of vanadium in water saturated quartz sand column perturbed with IS.

Factor	D (cm^2 min^{-1})	R	K (min^{-1})	R^2
Chloride	0.02549	–	–	–
IS = 0.001 M	–	12.19	0.05436	0.9855
IS = 0.01 M	–	16.89	0.005185	0.9961
IS = 0.1 M	–	15.31	0.00002035	0.9212

Table 4. The basic properties of mineral colloids.

Colloid	CFC (mmol kg^{-1})	Inflation times (mL g^{-1})	Specific surface (m^2 g^{-1})	Particle size (nm)
Kaolinite	102	1.25	12.42	814.5
Montmorillonite	1372	5.86	56.38	463.6

decrease of the IS could strengthen the sorption ability of vanadium onto the quartz sand. This could be attributed to the fact that the reduction of the interaction force between ion, the strength of the ionic activity coefficient and effective concentration, resulted in the retardation of vanadium as the IS decreased. When the electrolyte concentration increased to 0.1 M, electrostatic interactions between the VO_3^- anion and the quartz sand intensified, and most of the retained vanadium regulated by reversible equilibrium sorption and deposition in the columns were released back into the pore water, thus, exceeding to unity. Simulations of the transport model matched well with the experimental breakthrough data of V with R^2 from 0.9212 to 0.9855 (Table 3).

3.3. Effect of clay minerals on the transport of vanadium in water saturated quartz sand column

The transport of vanadium facilitated with montmorillonite colloids (V-MC) and kaolinite colloids (V-KC) were presented in Figure 3. Compared to the chloride, the beginning and ending time required for detection of the V-MC breakthrough curve point decreased compared with the vanadium and V-KC breakthrough curves. The montmorillonite colloids promoted the mobility of vanadium through the saturated quartz sand column. Specially, the montmorillonite colloid had a relatively high surface area (Table 4), which made the vanadium transport as a colloid-metal complex in the quartz sand column and thus had a strong ability to promote the transport of vanadium. Also, we found that montmorillonite had a stronger facilitated-transport effect than kaolinite to the vanadium. This may be caused by the different properties of the two colloids (Table 4). The higher critical flocculation concentration (CFC), inflation times and specific surface area of montmorillonite made it more stable on the quartz sand and easily disperse and

leach in the column. Simulations of the transport model matched well with the experimental breakthrough data of vanadium and colloid with $R^2 > 0.9$. Simulations of the transport model matched well with the experimental breakthrough data of vanadium and the colloid with $R^2 > 0.9$.

4. Conclusions

Laboratory column experiments were conducted to determine the effects of solution ionic strength (IS), pH and clay minerals on the transport of vanadium in water saturated quartz sand. Our results indicate that: (1) solution pH plays an important role in controlling the transport of vanadium, the mobility increases as the pH increasing from 4 to 8; (2) the mobility of vanadium is enhanced as the ionic strength(IS) increases; (3) the vanadium mobility in the column is promoted by montmorillonite more than kaolinite; and (4) traditional solute transport model can be used to simulate the retention and transport of vanadium in water-saturated porous media.

Notes on contributers

Yulu Wang was a MS Student of environmental science at the Northwest A&F University, China. Born, educated, and living in China.

Xianqiang Yin was an Associate Professor of environmental science at Northwest A&F University, China. He has published more than 20 articles. His research interests were biogeochemistry, environmental nanotechnology, transport of colloid and trace metals, and remediation of contaminated soil. Born, educated, and living in China.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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