



Effect of humic acid on uranium(VI) retention and transport through quartz columns with varying pH and anion type



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ABSTRACT

Humic acid (HA)¹ is ubiquitous in the environment and is an important factor in the migration behavior of U(VI) in the geological medium. The present work investigated the effect of HA on the migration behavior of U(VI) using quartz column experiments at different pH values and in the presence of various anions. The U(VI) adsorption characteristics and speciation were also studied to illuminate further the migration behavior of U(VI). Our results indicated that, at pH 6.0, HA slightly increased the migration velocity of U(VI) during the initial phase and reduced the quantity of eluted U(VI) because of the formation of HA-U(VI). The relative concentration (c/c_0) of U(VI) was higher in the HA-U system at pH 8.0 than that at pH 5.0 because of the higher solubility of HA in basic solutions and the difference in charge of HA-U(VI). In the U-HA-anion system at pH 6.0, the breakthrough pore volumes (PVs²) of U(VI) in electrolytes containing Cl⁻ and SO₄²⁻ anions (PV = 8) are much higher than for solutions containing phosphate (PV = 3), while the HA migration behavior was not significantly affected by the type of anion. Thus, the fast migration of U(VI) under HA and phosphate was attributed to phosphate rather than HA. This result suggests that phosphate should be given more attention in predictions of U(VI) migration, especially in regions with high groundwater phosphate content.

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1. Introduction

Uranium-contaminated soil and groundwater are widespread because of nuclear power plant operation, uranium mining, milling, enrichment, spent fuel reprocessing, and high-level waste disposal (Arai et al., 2006). It is important to assess the migration behavior and biotoxicity of uranium because of the danger posed by both the radioactivity and heavy-metal toxicity of this pollutant (Simon et al., 2003). The fate and transport of uranium in subsurface environments are controlled by its interactions with the environmental medium, which include redox reactions, dissolution and precipitation, and adsorption/desorption processes. Thus, many studies of the environmental factors affecting uranium migration, such as pH value, ionic strength, oxides, organic matters, microorganism, and colloids have been conducted (Fox et al., 2006; Nair

and Merkal, 2011; Uyuşur et al., 2015; Rout et al., 2015).

Humic substance (HSs³), such as humic acid and fulvic acid (HA/FA⁴) have been recognized as one of the most important factors in the migration of uranium because HSs are ubiquitous and heterogeneous macromolecules containing a suite of aliphatic, aromatic, carboxylic, hydroxyl, phenolic and thiosulfate functional groups (Cumberland et al., 2016). HSs have important effects on uranium sorption and migration because of their participation in solid-water interface reactions (Tinnacher et al., 2013; Stamberg et al., 2003; Luo and Gu, 2009; Manaka et al., 2008). HA is soluble in the pH range of natural water and is highly capable of complexing metal ions and forming colloids (Mibus et al., 2007). The effect of HA on the adsorption and migration of metal ions, metal oxides, and mineral colloid has been thoroughly researched (Artinger et al., 1998; Yoshida and Suzuki, 2006; Zhang et al., 2015; Lv et al., 2014; Li et al., 2013).

The influence of HA is crucial to uranium migration because of the interaction of HA with uranyl ions. The effects of HA on uranium

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Abbreviations

HA	Humic acid
PV	Pore volume
HS	Humic substance
FA	Fulvic acid
BTC	Breakthrough curve
DI	De-ionized

migration are complicated, and various conflicting conclusions have been reported: (i) HA can increase the migration velocity of uranium. Column experiments with Aeolian quartz sand and groundwater rich in humic colloids demonstrated that a certain fraction of the loaded uranium migrated as a humic colloid-borne species with a velocity up to 5% faster than the mean groundwater velocity (Artinger et al., 2002). The author attributed this phenomenon to a size exclusion process. (ii.) HA can decrease the uranium migration mass. It was reported that HA can retard uranium migration because the uranium that was associated with HA was immobilized by humic colloid filtration, producing a delay effect (Mibus et al., 2007). (iii.) The effect of HA on uranium migration behavior is limited. The behavior of uranium in soil containing natural organic material was not substantially influenced by additional HA (Liao et al., 2013). Therefore, the effects of HA should be investigated in more detail in surroundings involving geochemical factors, such as pH, ion type and concentration, organic matter, colloids, and flow rate conditions on uranium migration. The effect of HA in the presence of various cations has been previously investigated (Akbour et al., 2013; Cheng et al., 2016; Davis et al., 2002). However, to the best of our knowledge, no investigations of the effect of HA on the migration behavior of U(VI) in the presence of various anions currently exist.

The present study focused on the effect of anions and HA on the retention and transport of U(VI) during column tests, which were conducted at a constant injection rate. The migration character of U(VI) was studied in the presence and absence of HA. Quartz was selected as an adsorbent and column material because it is a common mineral in the Earth's crust and a typical constituent of granite and sandstone (Nair et al., 2014). The effects of environmental factors, such as pH and the type of anions on uranium sorption/transport, were considered. Breakthrough curves (BTCs)⁵ and retention profiles for various combinations of these factors were compared in the presence and absence of HA to illustrate the effect of HA on uranium migration. The mechanisms of HA affecting the uranium transport characters were discussed.

2. Materials and methods

2.1. Reagents

A stock solution of uranyl nitrate was prepared by dissolving uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in deionized (DI^6) water (conductivity > 18 $\text{M}\Omega \text{ cm}$). HA (CAS: 1415-93-6) was purchased from Aladdin Industrial Co. and used without pretreatment. Quartz was purchased from Rongsheng Science & Technology Co., Ltd and washed with DI water more than ten times. The chemical composition reported by the manufacturer was SiO_2 (>99.0%), chloride (<0.005%), Fe (<0.002%), and impurity resolved by HCl (<0.2%). All NaCl, NaHSO_4 , NaH_2PO_4 , and acids and bases used were of analytical purity and were used as supplied without further purification.

2.2. U(VI) sorption experiments

A batch study was performed to determine the effect of HA on U(VI) sorption on quartz. Quartz (1.0 g) was added into a polyethylene centrifuge tube (10 mL capacity) along with a certain volume of U(VI) stock solution, HA solution, and background electrolyte solution (NaCl , NaHSO_4 , NaH_2PO_4) to make a solution with a final volume of 6.0 mL. In our experiments, the concentration of U(VI) solution was fixed at 5.0 mg/L. A negligible volume of HCl or NaOH was added to adjust the pH to the desired value. The centrifuge tubes were shaken for ~24 h with incubation at 25 °C except thermodynamics test before they were centrifuged (4000 rpm, 10 min). The supernatant liquid was collected to measure the concentration of U(VI). The efficiency of U(VI) removal from aqueous solution by adsorption (Sorption, %) and the adsorption capacity of quartz (q_e , mg/g) were calculated according to Eqs. (1) and (2), respectively:

$$\text{Sorption} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C_0 and C_e (mg/L) are the initial and equilibrium liquid phase concentrations of U(VI), respectively. V (mL) denotes the volume of the U(VI) solution in the tubes, and m (g) denotes the amount of adsorbent.

2.3. Column transport experiments

Column experiments were performed in a polypropylene column ($\varnothing 25 \text{ mm} \times 100 \text{ mm}$). Quartz of approximately 20–40 mesh was packed in the column and supported on a Teflon filter (pore diameter of 5 μm). The resulting porosity of the porous media was determined to be 0.42. The injection solution was delivered by a 12-head peristaltic pump (Langer Pump Co. Ltd., China) in an upward direction at a flow rate of ~30 mL/h (Darcy flux of 6.1 cm/h). After the quartz column had been equilibrated with ~6 pore volumes (PVs^2) of DI water at the desired pH value, U(VI) solutions (10 PVs) with different contents and compositions of background electrolyte and HA were introduced to the column. Finally, ~6 PVs of DI water was flushed through the column to study the release of the retained U(VI) from the column. Before investigating the effect of HA in the presence of different anions, we investigated the individual effects of HA and the anions of interest on the U(VI) migration.

2.4. Measurement of U(VI) and HA

The concentration of U(VI) was determined by UV-Vis spectrophotometry (Shimadzu UV-1800, Japan) at 652 nm using the As(III) method (Li et al., 2016). The correlation coefficient of the standard curve was 0.999.

The HA concentration was also determined by UV-Vis spectrophotometry at 220 nm. The concentration of samples containing U(VI) and HA was calculated under the assumption that the absorbance at 220 nm was equal to the sum of the absorbance of HA and U(VI) and that HA did not impact the absorbance of U(VI) at 652 nm. The process for measuring the concentration of HA involved three steps: (1) Measuring the absorbance of U(VI) at 652 nm to determine the U(VI) concentration. (2) Calculating the absorbance of U(VI) at 220 nm. (3) Subtracting the absorbance of U(VI) from the total absorbance of a sample containing U(VI) and HA at 220 nm and constructing a linear relationship between the HA concentration and its absorbance. The correlation coefficients in

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