Interaction between uranium and humic acid (II): complexation, precipitation and migration behavior of U(VI) in the presence of humic substances (Postprint)

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Abstract

The complexation, precipitation, and migration behavior of uranium in the presence of humic acid (HA) or fulvic acid (FA) were investigated using cation exchange, ultrafiltration, and dynamic experiments, respectively. The results showed that (i) complexation equilibrium between uranium and humic substances was achieved at approximately 72 h, (ii) the coordination number varied from 1:1 to 1:2 (U(VI):humic acid) as pH increased from 3 to 6, and (iii) the complex stability constant decreased with increasing temperature but increased with pH value. We found that the precipitation of uranyl could only be observed in the presence of HA, and the precipitation was influenced by conditions such as pH, uranium concentration, temperature, and HA concentration. The maximum precipitation proportion of up to 60% could be achieved under the condition of a 40 mg/L HA solution at pH 6. We further observed that the migration behavior of uranium in soil in the presence of humic acid (HA) or fulvic acid (FA) differed from that in the presence of inorganic colloids, and the effect of humic substances (HS) was limited.

Full Text

Preamble

Interaction between Uranium and Humic Acid (II): Complexation, Precipitation and Migration Behavior of U(VI) in the Presence of Humic Substances

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Abstract

The complexation, precipitation, and migration behavior of uranium in the presence of humic acid (HA) or fulvic acid (FA) were investigated using cation exchange, ultrafiltration, and dynamic experiments, respectively. The results showed that (i) complex equilibrium between uranium and humic substances was achieved at approximately 72 hours, (ii) the coordination number varied from 1:1 to 1:2 (U(VI):humic acid) as pH increased from 3 to 6, and (iii) the complex stability constant decreased with increasing temperature but increased with pH value. We found that uranyl precipitation could only be observed in the presence of HA, and the precipitation was influenced by conditions such as pH, uranium concentration, temperature, and HA concentration. The maximum precipitation proportion of up to 60% could be achieved under conditions of 40 mg/L HA solution at pH 6. We further observed that the migration behavior of uranium in soil in the presence of humic acid (HA) or fulvic acid (FA) differed from that in the presence of inorganic colloids, and the effect of humic substances (HS) was limited.

Key words: Interaction, Uranium, Humic acid, Complexation, Migration, Precipitation, Soil

Introduction

Radioactive wastes and contamination were generated inevitably with the development of nuclear weapons, nuclear power, and other nuclear techniques. Typically, low-to-medium level or very-low-level radioactive waste materials were stored in shallow underground repositories with multiple barrier systems. Unfortunately, radioactive waste could be released into the environment if these barriers were damaged or lost efficacy. Additionally, wastes from operating nuclear facilities and decommissioned equipment could be directly released into the environment. For decades, safe treatment of radioactive wastes has been a major concern worldwide and remains in a continuously developing stage [1-5].

Investigation of radionuclide precipitation and migration behavior is vital for evaluating the long-term safety of underground repositories. As an important actinide, uranium can readily react with natural media, including inorganic and organic matter, due to its active chemical properties. This high reactivity influences the chemical species and behavior of uranium, which further affects its migration in the environment [6-8]. Thus, investigating the interaction between uranium and natural media, particularly natural organic matter, helps us better understand actinide transport in natural environments.

Among the many natural substances, humic substances (HS) account for more than 50% of natural organic materials and are widely distributed in soils, water, and ecosystem precipitates. HS are divided into fulvic acid (FA), humic acid (HA), and humin according to their molecular weight or solubility in different acidic solutions. FA consists of moderate-molecular-weight organic substances of non-specific composition and is soluble at all pH values. HA consists of high-molecular-weight organic substances that are soluble in alkaline media (e.g., 0.1 mol/L NaOH) but insoluble in acidic media (at pH 1-2). Humin is composed of portions of organic matter in soils or sediments and is insoluble at any pH value [8,9]. Among these substances, FA and HA actively interact with many metal ions, such as Cu(II), Ni(II), Co(II), Np(V), Am(III), Eu(III), and Cm(III), via adsorption [10], complexation [11-17], or redox reaction [18] through their functional groups, including carboxyl (-COOH), carbonyl (-CO), methoxy (-OCH_3), and hydroxyl (-OH).

The complexation of HS (including FA and HA) with rare metals, heavy metals, and actinides in groundwater, sediment, or synthetic systems has been widely studied using electrophoretic ion focusing [19,20], ion exchange [21], UV spectroscopy [22], time-resolved laser fluorescence spectroscopy (TRLFS) [23], ultrafiltration, and other methods [17]. Metal ion speciation in the presence of HS has also been investigated using mathematical models [24,25]. The complexation of natural humic substance colloids with metal ions in natural environments has been determined directly [26-29]. These experiments imply that complexation is an important factor influencing the migration or precipitation behavior of high-valent metal ions, in addition to adsorption and redox reactions [6-8,25,30,31]. Therefore, investigating the interaction between uranium and HS is significant for understanding the chemical behavior and speciation of uranium in soils or groundwater, which will not only help predict uranium transport in natural environments but also better guide safety evaluations for nuclear waste disposal.

In our previous paper, we discussed the adsorption of uranium on solid HA [32]. The experimental results showed that uranium could be adsorbed onto solid HA under certain conditions, and the adsorption was influenced by pH, temperature, origin of humic acid, and other factors [32]. In this paper, to further understand the interaction between uranium and HA, we investigated HS complexation with uranium using the Schubert method, and performed precipitation and migration experiments.

2.1 Materials

Soil samples [32] were dried at room temperature, ground, sieved to 2.0 mm after removal of plant roots, and sealed in polyethylene bags for use. Stock solution of U(VI) was prepared from uranyl nitrate ($(UO_2(NO_3)_2 \cdot 6H_2O)$), and its concentration was calibrated by mass analysis. Other chemical reagents were of analytical grade unless stated otherwise. Glassware was rinsed with distilled water and allowed to dry before use.

X-5 macroporous adsorption resin (surface area: 500-600 m^2/g; average pore diameter: 29-30 nm) purchased from The Chemistry Plant of Nankai University was refluxed with hot ethanol, then washed with cool ethanol and kept in ethanol for use. 001$×7*strongacidiccationexchangeresinwaspurchasedandpretreatedsequentiallywithHClandNaO* to Na^+ form before use. Centrifuge tubes with a molecular weight cutoff of 3 kD were obtained from Millipore Company. The 0.45 m microfiltration membrane was purchased from Shanghai Xinya Device Factory. Migration columns (Φ10$×$150 mm) were custom-made with plexiglass in our laboratory.

2.2 Measurement of U(VI)

The concentration of U(VI) in solution was determined directly by UV/Vis spectroscopy or Anodic Stripping Voltammetry. U(VI) in soil columns was determined after transformation into aqueous solution using the methods described below.

For UV/Vis spectroscopy, a 10 mL test solution digested with 0.8 mL of 30% H_2O_2 and 0.2 mL of 16 mol/L nitric acid was washed with 5 mL buffer solution (chloroacetic acid-sodium acetate, pH = 2.5) into a 25 mL volumetric flask. The final volume was increased to 25 mL with 1 mL of 0.6% arsenazo (III) aqueous solution and distilled water for determination by UV/Vis spectroscopy.

For soil samples, the sample was weighed and placed in a vessel, then digested with hot HCl (10 mL), HNO_3 (5 mL), and H_2SO_4 (1 mL). After complete evaporation, 20 mL of 40% HNO_3 was added to dissolve the residual salt. The solution was filtered through neutral filter paper, and the filtrate was separated using a TBP extraction resin chromatographic column. Finally, the eluted uranium solution was mixed with 2 mL of a mixture solution (25 g 1,2-cyclohexanediaminetetraacetic acid, 5 g NaF, and 65 g sulfosalicylic acid dissolved in 1 L of pH 8 NaOH solution) and adjusted to pH 7.

For very low uranium concentrations (< 1 g/L), the digested test solution was mixed with chloranilic acid solution for determination by Anodic Stripping Voltammetry.

2.3 Complexation Experiment by Cation Exchange Method

This method is based on retention of the polycation humate complex on the cation exchange resin while the non-complexed uranyl cation passes through [21]. A series of batch cation exchange experiments were performed to calculate the stability constant of UO_2^{2+} with HS.

All experiments were conducted at a total uranium concentration of 1.0 mg/L with 0.5 g of resin in each sample over a pH range from 3 to 6. Ionic strength of 0.10 was maintained using $NaClO_4$ solution, and pH was adjusted with dilute NaOH or HCl. The concentrations of HA and FA were varied from 5 to 10 ppm and 10 to 200 ppm, respectively. All experimental samples were kept in 30 mL vessels and shaken continuously for 96 h at steady-state temperature.

The aqueous U(VI) was then determined using UV/Vis Spectroscopy or Anodic Stripping Voltammetry as described above.

2.4 Precipitation Experiment

Ultrafiltration was used to separate free uranyl ions from uranium-HS precipitate. Free uranyl ions and micro-humic matter could pass through the filtration membrane, while complexed humate, macro-humic colloids, and HA with adsorbed U(VI) were retained on the membrane. Based on the orthogonal method used to determine optimum reaction conditions, further experiments were performed as follows: 20 mL of 10 mg/L uranyl nitrate solution was added to a 50 mL vessel containing HS and electrolyte solution. The required concentrations of HS and electrolyte were regulated, and the vessel was shaken. After shaking for 24 h, the reaction solution was filtered through a 0.45 m microfiltration membrane.

The residual U(VI) in the filtrate was tested, and the precipitation ratio was calculated using the following formula:

$$P\% = \frac{C_0 - C}{C_0} \times 100$$

where C_0 is original concentration of $UO_2{}^{2+}$ (mg/L), C is residue concentration of $UO_2{}^{2+}$ (mg/L), P% is the percent of U(VI) precipitate.

2.5 Migration Experiment

Migration experiments were carried out in plexiglass columns (Φ10$×150mm)pumpedat12mL/dwithgroundwat
cmthickslices, andtheconcentrationofUO_{2}$$^{2+}$ in soil was tested as described above. The water flow velocity in the experimental column was determined by the breakthrough curve of HTO, and ^{3}H in the outflow was analyzed with a liquid scintillation analyzer.

Migration results were expressed as the distribution coefficient (K_d), retardation factor (R_d), and maximum migration distance (d, mm):

$$R_d = \frac{\nu_w}{\nu_n} = 1 + \frac{\rho}{\varepsilon} K_d$$

where _w is the flow velocity of groundwater (cm/d), _n is the migration rate of U(VI) (cm/d),   is the effective porosity of the soil, and   is the bulk density of the soil (g/cm^3).

3.1 Complexation of U with HS

3.1.1 Equilibrium Time

The equilibrium time for complexation of UO_2^{2+} with HA or FA was obtained through time-dependent experiments. In this multicomponent system, equilibrium occurred through two processes: (i) ion exchange with cation exchange resin and (ii) complexation of U(VI) with HA or FA. During the first 32 h, ion exchange was the dominant process, resulting in a decrease of UO_2^{2+} in aqueous solution over time. After 32 h, complexation became dominant, and we observed an increase of UO_2^{2+} in aqueous solution until reaching a plateau at approximately 72 h. Therefore, 96 h was selected as the equilibrium time for complexation experiments with UO_2^{2+}.

3.1.2 Effect of pH on Complexation of UO_2^{2+} with HA or FA

The effect of pH on complexation was investigated from pH 3 to pH 6, with results shown in Fig. 1. The stability constant of complexation increased with pH from 3.0 to 6.0. This trend was most likely caused by release of H^+ from functional groups such as carboxyl and hydroxyl, which consequently facilitated combination of UO_2^{2+} with HS at high pH values. Conversely, HS dissociation was retarded by high H^+ concentration at low pH values, slowing the complexation of UO_2^{2+} with HS in aqueous solution. We found that the complexation tendency with HA was more pronounced than that with FA (Fig. 1).

3.1.3 Effect of Temperature on Complexation

Experimental results of complexation with HA and FA at different temperatures are shown in Fig. 2. The stability constant from 10°C to 20°C was clearly lower than that at higher temperatures from 30°C to 40°C. In the range of 0°C to 20°C, complexation stability decreased as temperature increased. However, from 30°C to 40°C, complexation stability increased with temperature. The reason might be that HA/FA complexed with uranium in its essential state at low temperatures (<20°C), but polymerized with each other before complexation at high temperatures (30-40°C). We believe this polymerization helps generate more stable complex compounds. The stability constant of HA was always higher than that of FA under these conditions, further supporting our speculation.

3.2 Precipitation

3.2.1 Determination of Influence Factors

The selection of influence factors on uranium precipitation in the presence of humic substances was performed using orthogonal experiments. An $L_{27}(3^{13})$ schedule was chosen for 7 factors and 3 levels . The orthogonal experiment results showed that the effect factors on precipitation in the presence of HA were, in decreasing order: pH, uranium concentration, temperature, and HA concentration. However, in the presence of FA, only temperature could influence precipitation. Based on these orthogonal experiments, the influencing factors for subsequent condition experiments were determined.

3.2.2 Effect of pH on Precipitation

Precipitation experiments were performed in a mixture solution of 10 mg/L uranium and 0.1 mol/L $NaClO_4$. pH efficiently influenced U(VI) precipitation in HA but had an indistinct effect in FA, as described in Fig. 3. This result was consistent with the orthogonal experiment findings. Furthermore, the precipitation percentage increased with pH from 3 to 6, but decreased with pH from 6 to 9. In other words, about 65% of uranyl humate was retained on the 0.45 m micropore membrane at pH 6, which is close to environmental pH conditions. However, as pH increased or decreased from 6, the precipitate gradually dissolved. In contrast, uranyl fulvate passed through the membrane at all pH values.

3.2.3 Effect of Uranium Concentration

The effect of uranyl concentration on precipitation was secondary to that of pH, with results plotted in Fig. 4. The curve implied that precipitation was uranium concentration-dependent. When uranium concentration was lower than 5 mg/L, the precipitation percentage increased with uranium concentration. However, from 5 mg/L to 100 mg/L, the precipitation percentage decreased with increasing uranium concentration. This was likely because the sample solution containing approximately 40 mg/L HA limited the complexation/adsorption capacity for uranium. As a result, the maximum precipitation (approximately 60%) occurred at a uranium concentration of 5 mg/L.

3.2.4 Effect of HA Concentration

The test was carried out under conditions of 10 mg/L uranium solution at pH 5, with results shown in Fig. 5. An apparent effect of HA concentration on uranyl humate precipitation was observed, but the effect was limited under conditions of pH 5, uranium concentration of 10 mg/L, and mixing for 1 day. As HA concentration increased to 40 mg/L, the precipitation percentage no longer varied, reaching a maximum of approximately 60%, consistent with the data above.

3.2.5 Effect of Ion Strength

Uranium precipitation was evidently influenced by ionic strength from 0 mol/L to 0.5 mol/L, which was used to adjust ionic strength while maintaining 40-50% HA precipitation proportion. The data are plotted in Fig. 6.

3.3 Migration of Uranium in Soil

Nuclide migration is a key issue for radioactive contaminants in the environment and is affected by many factors. This study focused on the influence of different humic substances on uranium migration in soil. To understand the different effects of organic versus inorganic colloids on migration, $Fe(OH)_3$ and montmorillonite colloids were also investigated. Therefore, FA, extracted HA (EHA), purchased HA (PHA), $Fe(OH)_3$ colloid solution, and montmorillonite colloid solution were mixed with original soil in specific proportions, and all were tested simultaneously.

Before uranyl migration experiments, three columns were randomly chosen from the total samples for determination of water flow velocity using ^{3}H (Fig. 7). The three outflow curves coincided exactly, and the outflow velocity was calculated using a method developed by Liu et al. [33]. Under these experimental conditions, the average water flow velocity was calculated as 1.39 cm/d.

The curves for uranium migration in soil containing different colloids are depicted in Figs. 8a-f, and migration parameters are reported in . According to the migration data, additional FA could accelerate uranyl ion migration velocity, while EHA and PHA retarded the velocity compared to uranyl in original soil under these experimental conditions. However, despite the fact that FA (but not EHA or PHA) could transport uranyl farther from the origin, the combination of HA and uranium was still limited, and most uranyl humate remained at the original point. The retardation by EHA or PHA could be related either to the adsorption described in our previous paper [32] or to HA complexation. The uranyl humate groups formed through these reactions were too large to pass freely through soil pores. In contrast, $Fe(OH)_3$ and montmorillonite accelerated uranyl migration because of their micro-complex compounds, compared with the effect of inorganic colloids on uranyl migration in soil. In general, additional HA had almost no effect on U(VI) migration in soil, unlike inorganic colloids.

4 Conclusion

Humic substances could complex with UO_2^{2+}, but the reaction was influenced by pH and temperature, and the complex compounds were unstable. Under different conditions, UO_2^{2+} could complex with HS in different ligand numbers such as 1:1 or 1:2 or more.

We also found that, influenced by humic substances, UO_2^{2+} could be present in different speciation in soil. However, under conditions of 40 mg/L uranium solution at pH 6 (I = 0.1 mol/L, T = 30°C), approximately 60% of precipitate was retained by the 0.45 m micropore membrane, although this is much smaller than natural soil pores (which are around 1 m). Moreover, precipitation behavior was also influenced by pH, uranium concentration, HA concentration, and temperature, in that order.

In short, due to adsorption and complexation of uranium with HS, the behavior of UO_2^{2+} containing natural organic material (NOM) was influenced by additional HS. However, this effect was limited and could not generally change the migration state. The effect of other factors on uranium migration in soil will be further investigated in future work.

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Note: Figure translations are in progress. See original paper for figures.