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Spectroscopic study on the role of TiO_2 in the adsorption of Eu(III) and U(VI) on silica surfaces in aqueous solutions

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ABSTRACT

To determine the effects of TiO_2 on the adsorption of actinides onto mineral surfaces in groundwater, silica was partially coated with TiO_2, and Eu(III) and U(VI) were individually adsorbed from separate 0.1 mM concentration solutions. The TiO_2-coated silica showed higher Eu(III) and U(VI) adsorption capacities for increasing amounts of TiO_2 coated on the silica surfaces, and thus the existence of TiO_2 can decrease the mobility of Eu(III) and U(VI) contaminants.

In luminescence studies, it was found that TiO_2 considerably enhanced the luminescence of the adsorbed Eu(III) indicating that TiO_2–Eu(III) forms surface complexes which may decrease the number of water molecules at the inner sphere of Eu(III), but this was not observed for U(VI). An energy transfer from the TiO_2 to the Eu(III) was confirmed in this case of amorphous TiO_2-coated silica in Eu(III) solutions, and an increase of the luminescence lifetime of Eu(III) for increasing concentrations of coated TiO_2 was also observed.

1. Introduction

The adsorption of inorganic ions on solids is important in the decontamination of liquid waste repositories [1]. In particular, the adsorption of toxic and radioactive contaminants on immobile minerals retards their transport in groundwater, which is a public health concern [2]. The adsorption of uranium and americium (or curium) onto silicate, which is found in the majority of the Earth's crust, can be considered one of the significant reactions affecting the transport of actinides in the environment [3]. In addition, titanium dioxide (TiO_2) is a well-known mineral existing in soils and sediments. The aim of this paper is therefore to study the adsorption of Eu(III) (which is a chemical analogue of Am(III) and Cm(III)) and U(VI) from aqueous solutions onto TiO_2-coated silica, to understand the radionuclide migration occurring in the groundwater of natural environments.

The effects of Fe(III)- or Ti(IV)-ions on the adsorption behaviors of Eu(III) onto silica surfaces in aqueous solutions were partially investigated in our previous published paper [4]. Herein, the adsorption of Eu(III) from aqueous solutions on TiO_2-coated silica is further discussed for comparison with the results from U(VI).

2. Experimental

The chemicals used in this study, including silica (Sigma–Aldrich Corporation; particle size 40–63 μm; surface area 550 m^2/g), titanium(IV) butoxide [$Ti(OBu)_4$], ethanol [C_2H_5OH], toluene [$C_6H_5CH_3$], europium(III) oxide [Eu_2O_3], and uranyl [UO_2^{2+}] solution were all of high purity and used as received. Perchloric acid [$HClO_4$], sodium perchlorate [$NaClO_4$], and sodium hydroxide [NaOH] were of analytical grade. The NaOH solution was titrated with a standard solution of 0.1 M hydrochloric acid [HCl] (Merck & Co., Inc.) in the presence of a phenolphthalein indicator.

The dry silica was dispersed in 3.7 M HNO_3 for one day and washed with distilled water until the wet silica surface became neutral. Finally, the resulting silica was dried in an oven at 120 °C for 6 h and stored in a capped bottle after cooling.

11.3 mM Eu_2O_3 in 20.62 mM $HClO_4$, and 10.01 mM UO_2^{2+} in 16.05 mM $HClO_4$ were prepared as stock solutions for the Eu(III) and U(VI) adsorption tests. The metal-ion concentrations of the stock solutions were determined using inductively coupled plasma–atomic emission spectrometry, ICP–AES (ULTIMA 2C, HORIBA Jobin Yvon, HORIBA Ltd.) before dilution for the adsorption experiments. All of the solutions were handled under a nitrogen gas flow.

2.1. Partial TiO_2 coating on silica surface

$Ti(OBu)_4$ was slowly added to each silica sample (15 g) by stirring in a C_2H_5OH and $C_6H_5CH_3$ (1:1) mixed solution until

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various concentration of 0, 5, 10, 20, 100, and 200 mM of TiO_2 had been added to the 50 mL total solutions. Each mixture was then stirred for 2 h. The partially TiO_2-coated silica was glass filtered, washed with a C_2H_5OH and $C_6H_5CH_3$ (1:1) mixed solution three times, and dried in sequence at 120 °C for 6 h. X-ray diffraction (XRD) spectra (Siemens, D5000) of those samples were obtained to check any possible crystallinity, and the coated Ti(IV) concentrations were analyzed by ICP–AES after the samples were completely dissolved in a strong acid.

2.2. Eu(III) and U(VI) adsorption onto TiO_2-coated silica

In each test, 500 mg of differently TiO_2-coated silica was placed in a 50 mL solution consisting of either 0.1 mM Eu_2O_3 in 18 mM $HClO_4$ or 0.10 mM UO_2^{2+} in 0.16 mM $HClO_4$, with 0.1 M $NaClO_4$ to control ionic strength. At this point, to observe the pH-dependent adsorption, 0.1 M NaOH was properly added to each mixture under a N_2 gas flow to eliminate the remaining CO_2 in the solution, and the pH increased between 8 and 7 for the Eu(III) and U(VI) adsorption tests, respectively. The mixture in each polyethylene beaker was stirred for more than 30 min until the pH equilibrium was achieved. Adsorbed and desorbed metal concentrations were then analyzed by ICP–AES after being filtered through a 0.1-μm pore-sized membrane filter.

2.3. Luminescence spectra and lifetime measurements of Eu(III) and U(VI) on TiO_2-coated silica in aqueous solutions

The luminescence spectra and lifetime of Eu(III) and U(VI) on the TiO_2-coated silica were directly obtained from the sediments in aqueous solutions. The luminescence spectra and lifetime measurements were performed at certain pH ranges in which the maximum adsorptions of Eu(III) and U(VI) were observed. The Eu (III) maximum was at pH 7, and U(VI) was at pH 5, as shown in the pH-dependent adsorption graphs of Fig 1.

Conventional spectrofluorimetry (AMINCO Bowman Series 2, SLM-AMINCO Spectronic Instruments) and time-resolved laser fluorescence spectroscopy (TRLFS) were adopted to measure the luminescence spectra and lifetimes. A pulsed Nd:YAG laser beam (Minilite, Continuum) at 266 nm and an optical parametric oscillator beam (Vibrant HE 355 LD, Opotek) at 394 nm were used as excitation sources for measuring the luminescence of U(VI) and Eu(III), respectively. Both lasers operated at a repetition rate of 10 Hz with average pulse energy of 1.3 mJ. Luminescence spectra were obtained using a gated-ICCD (intensified charge-coupled device, DH-720/18U-03 iStar 720D, Andor) attached to a spectrometer (SR-303i-A, Andor) at the gate delay time of 1 μs and gate width of 500 μs. Luminescence lifetimes were measured using a PMT (photomulitiplier tube, R928, Hamamatsu Photonics) attached to a Czerny–Turner type monochromator (iHR320, Horiba Jobin Yvon) and digital oscilloscope (DPO 4102B, Tektronix).

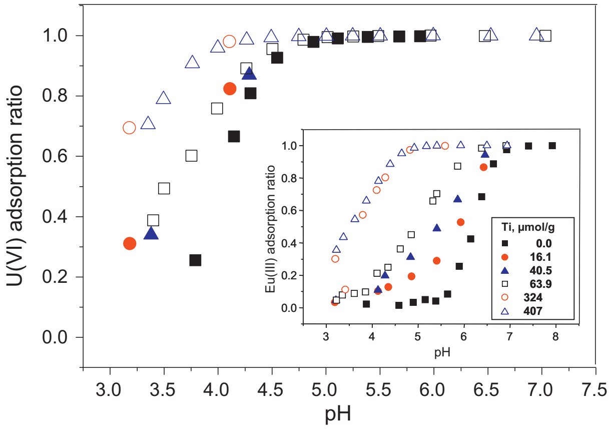

Fig. 1. pH dependence of the U(VI) and Eu(III) adsorption (with insert adopted from Ref. [4]) on partially TiO_2-coated silica according to the amount of TiO_2 coating, in 0.10 mM U(VI) or 0.1 mM Eu(III) solutions (500 mg of dissimilar TiO_2-coated silica in 50 mL of U(VI) or Eu(III) solutions).

3. Results and discussion

Totals of 0, 16.1, 40.5, 63.9, 324, and 407 μmol/g (Ti/silica) TiO_2-coated silica were obtained by the addition of the appropriate amount of $Ti(OBu)_4$. Further preparation and analysis methods were described in a previous paper [4]. The TiO_2-coated silica was confirmed by XRD spectra to be typical of amorphous materials with no crystalline particle structure.

Fig. 1 shows that the adsorption of U(VI) on TiO_2-coated silica has been enhanced by increasing the amount of coated TiO_2 on the silica surfaces, and the adsorption edges have been lowered a little, through the chemical interactions between U(VI) and the surface of the TiO_2. Here, adsorption ratio is defined as the adsorbed metal ion concentration on TiO_2-coated silica versus the initial metal ion concentration, and the adsorption edge is the value of pH at which the adsorbed metal ion quantity is approximately 50% of the initial concentration. As shown in the inserted graph of Fig. 1, similar results were observed in the case of Eu(III) adsorption on TiO_2-coated silica [4], except for a slightly different adsorption drift in the adsorption ratio according to the pH variation for the silica with less TiO_2 coating, and adsorption edges appear at a higher pH than those for U(VI) adsorption on TiO_2-coated silica.

Between pH 2.5 and 5, the adsorption processes may involve the combination of the hydrolysis of UO_2^{2+} and the adsorption of UO_2^{2+} and the hydrolysis products, $UO_2(OH)^+$ and $(UO_2)_2(OH)_2^{2+}$, based on the UO_2^{2+} species distribution diagram [5]. The TiO_2-coated silica with various TiO_2 coating concentrations was prepared using the hydrolysis and condensation of commercial silica and titanate precursors, and microporous sorbents such as the silica and titania can complex the ions on the outer surfaces. The hard Lewis acid of UO_2^{2+} forms more stable complexes with the hydroxyl ligands on relatively harder TiO_2 than those on SiO_2.

For Eu(III), the main luminescence spectra were the emissions associated with the $^5D_0 \rightarrow {}^7F_J$ ($J = 0–4$) transitions. The strongest emission peaks were observed in the range of $^5D_0 \rightarrow {}^7F_{1,2,4}$ transitions, and particularly the $^5D_0 \rightarrow {}^7F_2$ transition was hypersensitive [6,7]. The luminescence spectra of Eu(III) on partially TiO_2-coated silica, excited at 394 nm, were scanned from 550 to 650 nm, as shown in Fig. 2(a), and the peaks at 591 nm and 614 nm correspond to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, respectively. The peak corresponding to the $^5D_0 \rightarrow {}^7F_0$ transition, which indicates the absence of a high symmetry of Eu(III) structure [8], was also observed at 579 nm owing to the interaction of Eu(III) with titanol or silanol groups. It can be seen from Fig. 2(a) that the intensity of Eu(III) emission increases with the concentration of TiO_2 coated on silica. This result indicates that the interactions between Eu(III) and coated TiO_2 lead to an improvement of the TiO_2–Eu(III) surface complexes. As a result, stronger luminescence intensities were observed with increasing TiO_2 concentrations, because TiO_2 plays a role in the formation of complexes with Eu(III) on the TiO_2-coated silica [9].

However, U(VI) luminescence decreased with an increased amount of coated TiO_2, even though the spectral shape (position of peak wavelengths and ratio of peak intensities) of the excitation and luminescence spectra did not change. The decrease in luminescence intensity for U(VI) in Fig. 2(b) may be explained in terms of the quenching effect owing to the steric hindrance of hydrolyzed U(VI) [8].