Effect of pH, humic acid and addition sequences on Eu(III) sorption onto γ-Al₂O₃ study by batch and time resolved laser fluorescence spectroscopy

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HIGHLIGHTS

- Sorption of Eu(III) on Al₂O₃ is studied by batch and TRLFS technique.
- Effect of HA/Eu(III) addition sequences on Eu(III) was compared.
- The species of Eu(III) on HA–Al₂O₃ hybrids were studied by TRLFS.
- The interaction mechanism of Eu(III) with HA, Al₂O₃ and HA–Al₂O₃ was discussed.

GRAPHICAL ABSTRACT
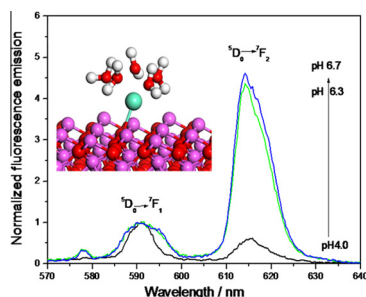
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ABSTRACT

To contribute to the comprehension of Eu(III) sorption properties in oxide-organic material systems, the influence of humic acid (HA) on Eu(III) sorption on bare and HA-bounded γ-Al₂O₃ is studied using batch experiments and time resolved laser fluorescence spectroscopy (TRLFS). The effect of pH and addition sequences of Eu(III)/HA/Al₂O₃ on Eu(III) sorption is carried out at different experimental conditions, and the results show that the sorption of Eu(III) is strongly dependent on pH and ionic strength. The sorption of Eu(III) is mainly dominated by ion exchange or outer-sphere surface complexation at low pH, and by inner-sphere surface complexation at high pH values. The presence of HA enhances Eu(III) sorption at low pH, but reduces Eu(III) sorption at high pH values. The addition sequences of Eu(III)/HA to alumina suspensions do not affect Eu(III) sorption, which is also evidenced by the TRLFS measurements. The surface complexes are characterized by their emission spectra [the ratio of emission intensities of $^5D_0 \rightarrow {}^7F_1$ ($\lambda = 594$ nm) and $^5D_0 \rightarrow {}^7F_2$ ($\lambda = 619$ nm) transitions] and their fluorescence lifetime. The TRLFS results show clearly that no effect of addition sequences on the sorption and speciation of Eu(III) in HA–Al₂O₃ hybrids after equilibration. These findings on the effect of humic substances in the complexation properties of Eu(III) indicate that the clarification of the environmental behavior of humic substances is necessary to understand the physicochemical properties of Eu(III), or its analog trivalent lanthanide and actinide ions in the natural environment.

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1. Introduction

Sorption behavior of a radionuclide on solid particle surfaces is a major process controlling the diffusion, migration, mobility and bio-availability of the radionuclide in the natural environment. The knowledge of the properties of trivalent lanthanide and actinide ions as fission products at the earth's surface is of great importance in the evaluation of the physicochemical behavior of long-lived actinide and lanthanide ions such as $^{152+154}$Eu(III), ^{243}Am (III) and ^{244}Cm(III) [1–4]. The complexation of trivalent lanthanide and actinide ions with humic acid has been investigated extensively by different methods [5–7]. The highly sensitive modern spectroscopic methods have been recently applied for the complexation and sorption study of lanthanide and actinide ions with humic acid and oxides [8–11]. However, the chemical mechanisms governing radionuclide immobilization are still not well understood. A mechanistic understanding of chemical speciation is necessary for long-term performance assessment of a nuclear waste repository.

In consideration of the effect of humic substances on the sorption or species of radionuclides, emphasis is sometimes placed on their role in extracting radionuclide from the aqueous solutions, because humic substances can form stable complexes with radionuclides in solution. From the literature survey, the presence of humic acid (HA) generally increases the sorption of metal ions at the mineral surface at acidic pH values but reduces the metal ion sorption at high pH values [8,12,13]. The increase of sorption is explained by the sorption of HA onto mineral surface followed by the interaction of metal ion with surface adsorbed HA, whereas the reduction of sorption is attributed to the formation of soluble M–HA complexes which stabilize the metal ion in aqueous solution because the sorption of negatively charged HA onto the negative charged surface of minerals decreases at higher pH values. Takahashi et al. [14,15] studied the effect of fulvic acid on the sorption of Eu(III) and Cm(III) onto montmorillonite by using laser induced fluorescence spectroscopy, and they found that Eu(III) and Cm(III) can be adsorbed as An(III)-fulvate complex in the FA-montmorillonite hybrids. Montavon et al. [8] studied the effect of polymaleic acid on Eu(III) sorption to alumina and found that the species of Eu(III) in such ternary system was governed by both humic substance adsorbed on the mineral surface, the free humic substance in solution and the surface properties of mineral particles. In our previous studies [13,16], we also found that the presence of humic substances enhanced Eu(III) sorption at low pH but reduced Eu(III) sorption at high pH values, which were in good agreement with the references mentioned above. However, we also found that the presence of humic substances decreases the sorption of heavy metal ions on carbon nanomaterials, which was attributed to the high specific surface areas and large amounts of oxygen-containing functional groups on nanomaterials [17]. Although the interaction mechanism of radionuclides can be evaluated from the sorption curves using surface complexation modeling, the local structures, especially the species of surface adsorbed radionuclides on solid particle surfaces are still not clearly achieved, which is crucial to evaluate the physicochemical behavior of radionuclides at solid-water interfaces.

Time resolved laser fluorescence spectroscopy (TRLFS) is a useful method for investigation the local structures of Eu(III) in various systems, since it is highly sensitive and selective for Eu(III) species by the f-f transitions of Eu(III) fluorescence, providing valuable information on their local structures at molecular level [18,19]. With TRLFS analysis, the number of water molecules in the first coordination sphere can be determined from the lifetime of the fluorescence, and the species can be achieved by comparing the fluorescence spectra. Moreover, the method can be applied to surface adsorbed species at the solid-water interface even in the presence of water, i.e., samples do not need to be dried before analysis. This is an important advantage because the drying process may alter the surface adsorbed species on the solid surface. The TRLFS method has been used widely to study the solution chemical behavior of Eu(III) sorption onto bentonite [9], γ-Al$_2$O$_3$ [16,20] and montmorillonite [15], and the species of Eu(III) are evaluated from the results. Besides TRLFS, XPS and EXAFS can also provide useful information of metal ions on solid particles. The XPS spectrum can provide the oxidation state, chemical composition and bonding relationships for surface and near-surface elements, and the contribution of functional groups on the binding of metal ions. From the EXAFS analysis, one can get the information of the bond distance and coordination number of metal ions at molecular level, which is useful to understand the interaction mechanism and microstructure of metal ions on solid particles [1,21,22]. The TRLFS, XPS and EXAFS techniques are useful methods to understand the interaction of metal ions at solid-water interfaces.

Although the sorption of Eu(III) on Al$_2$O$_3$ has been studied extensively using different methods [3,16,20], the addition sequences of Eu(III) and HA on Eu(III) sorption is still scarce, especially the spectroscopy analysis at molecular level. In this study, we studied the sorption of Eu(III) on Al$_2$O$_3$ particles at different experimental conditions. Effects of pH, ionic strength and addition sequences of HA/Eu(III)/Al$_2$O$_3$ on Eu(III) sorption were studied in detail. The TRLFS was applied to characterize the sorption of Eu (III) on Al$_2$O$_3$ and Al$_2$O$_3$–HA hybrids to investigate the sorption species. The lifetime and spectra of fluorescence of Eu(III) complex with HA were also characterized as a comparison. The results are important to understand the physicochemical behavior of Eu(III) at oxide-water interfaces in the natural environment.

2. Experimental

2.1. Materials

The hydrous γ-Al$_2$O$_3$ particles used in this work (Degussa, Aluminium Oxide C) have already been studied in sorption experiments by other authors [8,16,20]. Prior to its use, γ-Al$_2$O$_3$ was purified as follow: first washed with 0.1 M HNO$_3$, then with 0.1 M NaOH up to pH 10 and finally rinsing with Milli-Q water until the conductivity of the washing solution reached that of pure water. The purified alumina was then stored as a suspension (66 g/L) in Milli-Q water. The N$_2$-BET specific surface area was measured to be 105 m^2/g and the average particle radius measured by PCS was ∼150 nm.

The humic acid was isolated from the soil sample of Hua-Jia ridge (which is very near to the potential nuclear waste repository in China) of Gansu province (China) and was characterized in detail [23]. The main components are C 60.4%, H 3.5%, N 4.2%, O 31.3% and S 0.5%. The ^{13}C NMR spectroscopy analysis showed the main groups were aliphatic, carbohydrate, aromatic and carboxylate groups.

2.2. Sorption process

The sorption experiments of $^{152+154}$Eu(III) onto Al$_2$O$_3$ were carried out using batch technique under N$_2$ conditions. The experiments were carried out in N$_2$ globe box to avoid the influence of O$_2$ or CO$_2$ on the species of $^{152+154}$Eu(III). The stock suspension of Al$_2$O$_3$ (66 g/L) and NaClO$_4$ solution were first equilibrated for 2 days to achieve the interaction equilibration of Na$^+$ with Al$_2$O$_3$, and then the $^{152+154}$Eu(III) stock solution was added into