



Determination of colloidal pyrolusite, Eu(III) and humic substance interaction: A combined batch and EXAFS approach



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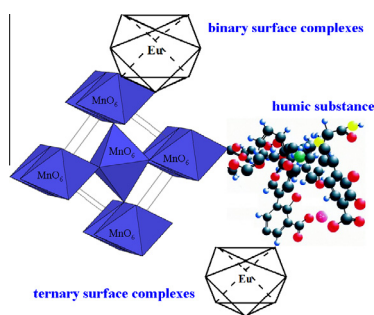
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HIGHLIGHTS

- HA or FA promoted Eu(III) interaction at low pH values.
- HA or FA reduced Eu(III) interaction at high pH values.
- Binary surface complexes and ternary surface complexes of Eu(III) can be simultaneously formed by EXAFS study.
- The findings are important to understand Eu(III) physicochemical behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

This work determined the role of humic acid (HA) and fulvic acid (FA), which was extracted from the natural soil, in the interaction mechanism and microstructure of Eu(III) with pyrolusite (β -MnO₂) by using batch experiments and extended X-ray absorption fine structure (EXAFS) techniques. We combined macroscopic and spectroscopic approaches to see the evolution of the interaction mechanism and microstructure of Eu(III) with β -MnO₂ in the presence of HA or FA in comparison with that in the absence of HA or FA. The results suggested that Eu(III) interaction with β -MnO₂ was obviously affected by the addition of HA or FA. The interaction of Eu(III) with β -MnO₂ was enhanced at pH < 6.5 in the presence of HA or FA, while Eu(III) interaction with β -MnO₂ was reduced at pH > 6.5 in the presence of HA or FA. The EXAFS fitting results provided a molecular evidence for the findings from the batch experiments. Adsorption of HA or FA onto β -MnO₂ greatly modified the microstructure of Eu(III) onto β -MnO₂. Only binary surface complexes of Eu(III) can be formed onto β -MnO₂ in the absence of HA or FA, while both binary surface complexes and ternary surface complexes of Eu(III) can be simultaneously formed onto β -MnO₂ in the presence of HA or FA, which was mainly responsible for the enhanced Eu(III) uptake at low pH values. The results observed in this work are important for the evaluation of physicochemical behavior of long-lived radionuclides (lanthanides and actinides) in the natural soil and water environment.

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1. Introduction

Interfacial behavior of long-lived radionuclides (lanthanides and actinides) at the natural particles (metal oxides and clay minerals)/water interface is quite important for the long-term performance assessment of nuclear waste repositories [1,2]. It is well known that Eu(III) is a trivalent lanthanide and can be regarded as a chemical homologue of trivalent actinides because the interfacial behavior of trivalent lanthanides and actinides is quite similar. Therefore, the interaction and microstructure of trivalent lanthanides and actinides at the natural particles/water interface can be simulated by using Eu(III) [3–7]. In this respect, a variety of studies have been conducted to investigate the interfacial interaction and microstructure of Eu(III) at the oxide/water and clay mineral/water interface mainly by a combination of macroscopic and spectroscopic techniques [1–11]. It was reported that extended X-ray absorption fine structure (EXAFS) technique is very useful to study the interfacial interaction and microstructure of Eu(III) with the solid particles at a molecule level. Nevertheless, the energy resolution of conventional EXAFS technique with solid-state detector (SSD) is no less than 120 eV, making it impossible to discriminate the $L\alpha_1$ fluorescence peak (~ 5849 eV) of Eu from the $K\alpha$ fluorescence peak (~ 5900 eV) of Mn [12–14]. Thus, it is hardly to investigate the interaction and microstructure of Eu(III) with Mn-bearing mineral.

Manganese (Mn) is one of the most abundant elements in the natural environment, which can be easily oxidized, leading to a variety of Mn (hydr)oxides (α - MnO_2 , α - $MnOOH$, δ - MnO_2 , δ - $MnOOH$, β - MnO_2 , γ - $MnOOH$). These Mn (hydr)oxides occur as fine-grained aggregates, marine, veins and fresh-water nodules and coatings on other solid particles and rock surfaces. Besides, these Mn (hydr)oxides are chemically active with large surface area, and negative over a wide range of pH. So, Mn (hydr)oxides are strong sequesters of heavy metal ions and radionuclides in the natural water and soil environment [15–17]. As a result, great attention has been paid to the interaction and microstructure of heavy metal ions and radionuclides, such as Np(V), Pu(VI), Zn, Cd and UO_2^{2+} with Mn (hydr)oxide [16–20]. For example, Nitsche and co-workers studied the interaction and microstructure of Np(V)/Pu(VI) at manganite/water and hausmannite/water interface, and it was reported that inner-sphere complexation were the main mechanism responsible for the interaction [16,17]. The interaction and microstructure of Cd(II) and Zn(II) at the γ - $MnOOH$ /water interface studied by EXAFS showed that Cd(II) interacted with γ - $MnOOH$ surface by the formation of mononuclear inner-sphere complexes [19], while Zn(II) interacted with γ - $MnOOH$ surface by the formation of multinuclear inner-sphere complexes [20]. However, because of the overlap of Mn $K\alpha$ fluorescence line and Eu $L\alpha_1$ fluorescence line, the interactions and microstructure of Eu(III) with Mn (hydr)oxide can be hardly studied by EXAFS.

In order to study the interaction mechanism and microstructure of Eu(III) at the Mn (hydr)oxide/water interface, it is quite necessary to develop new EXAFS technique with much higher energy resolution. In this respect, a bent crystal spectrometer based on the Rowland circle geometry, the energy resolution of which is greatly improved, can be utilized to selectively extract the fluorescence signal from Mn $K\alpha$ line to Eu $L\alpha_1$ line [12–14]. Using this new detector, Rakovan et al. [12] successfully collected the Eu L_3 X-ray absorption near edge structure (XANES) spectrum from a Mn- and REE-rich apatite sample, and studied the valence state of Eu in this sample. As the energy resolution of this bent crystal spectrometer is enhanced, the Eu $L\alpha_1$ fluorescence line and the Mn $K\alpha$ fluorescence line can be easily resolved [21]. So, we can obtain the EXAFS spectrum in a Mn-bearing samples to study the interaction

and microstructure of Eu(III) at the Mn-bearing mineral/water interface. In our previous reports [22,23], this high resolution EXAFS technique with a bent crystal analyzer was used to study the interaction mechanism and microstructure of Eu(III) at the β - MnO_2 /water and γ - $MnOOH$ /water interface as a function of solution pH, contact time, and reaction temperature.

In addition, Humic Substances (HSs), such as fulvic acid (FA) and humic acid (HA), which are widely present in natural water and soil environment, contain a large number of O-containing functional groups [24,25]. Because of these O-containing functional groups, FA and HA show strong interaction with lanthanides and actinides in natural environment, greatly affecting the fate and transport of lanthanides and actinides. So, the role of FA and HA in the interaction and microstructure of Eu(III) at the natural minerals/water interface is of particular interest [3–6,9–11]. It was generally regarded that FA and HA enhanced Eu(III) interaction with minerals at low pH values, whereas Eu(III) interaction decreased at high pH values in the presence of FA or HA [3–6,9–11]. However, to the best of our knowledge, no efforts have been focused on illustrating the role of FA and HA in the interaction and microstructure of Eu(III) at the Mn (hydr)oxide/water interface at molecular level.

Herein, the main objective of this paper was to determine the role of HA and FA in Eu(III) interaction and microstructure in aqueous pyrolusite (β - MnO_2) suspensions by batch and extended X-ray absorption fine structure (EXAFS) investigations. This paper highlights that the interaction of HA and FA with natural minerals can greatly change the interaction and microstructure of Eu(III), thus controlling the fate and transport of trace radionuclides (lanthanides and actinides) in heterogeneous aquatic environments.

2. Materials and methods

2.1. Chemicals and materials

The radiotracer $^{152+154}Eu(III)$ with a radionuclidic and radiochemical purity of 99.0% was purchased as the form of Eu_2O_3 from the China Institute of Atomic Energy (Beijing, China) [26]. Eu(III) stock solution was prepared from Eu_2O_3 after dissolution, evaporation and redissolution in 10^{-3} mol/L $HClO_4$. The detailed information of the extraction and characterization for fulvic acid (FA) and humic acid (HA) has been provided in previous investigations [3–6]. The preparation and characterization of the adsorbent pyrolusite (β - MnO_2) was described in our previous reports [22,24]. All other chemicals and reagents used were purchased in analytical purity and without further purification. The solutions in all experiments were prepared by Milli-Q water.

2.2. Batch interaction experiments

Batch interaction experiments were conducted under N_2 conditions in $NaClO_4$ solutions. The stock solutions of 0.5 g/L β - MnO_2 and 0.01 mol/L $NaClO_4$ in 10 mL polyethylene centrifuge tubes were pre-equilibrated for 5 h before addition of Eu(III) stock solution at $T = 20 \pm 1$ °C. Then, Eu(III) stock solution (including trace quantities of the radiotracer $^{152+154}Eu(III)$) and HA or FA stock solution were added the polyethylene centrifuge tubes to obtain the desired concentrations of different components. The suspension pH was adjusted by using 0.01 mol/L $HClO_4$ or NaOH solutions. The suspensions were gently shaken for 2 days to obtain adsorption equilibrium, and the solid was separated from the solution by centrifugation at 18000 rpm for 30 min. The concentration of $^{152+154}Eu(III)$ in supernatant was determined by liquid scintillation counting (Packard 3100 TR/AB Liquid Scintillation analyzer, PerkinElmer) with an ULTIMA GOLD ABTM (Packard) Scintillation

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