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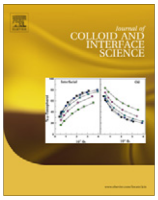

# Eu(III) uptake on rectorite in the presence of humic acid: A macroscopic and spectroscopic study

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ABSTRACT

This work contributed to the comprehension of humic acid (HA) effect on Eu(III) uptake to Na-rectorite by batch sorption experiments, model fitting, scanning electron microscopy, powder X-ray diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and extended X-ray absorption fine structure (EXAFS) spectroscopy. At low pH, the presence of HA enhanced Eu(III) sorption on Na-rectorite, while reduced Eu(III) sorption at high pH. The experimental data of Eu(III) sorption in the absence and presence of HA were simulated by the diffuse-layer model well with the aid of FITEQL 3.2 software. The basal spacing of rectorite became large after Eu(III) and HA sorption on Na-rectorite. Some of Eu(III) ions and HA might be intercalated into the interlayer space of Na-rectorite. EXAFS analysis showed that the $R_{Eu-O}$ (the bond distance of Eu and O in the first shell of Eu) and *N* values (coordination number) of Eu(III)–HA-rectorite system were smaller than those of Eu(III)-rectorite system.

## 1. Introduction

With the development of nuclear energy and proceeding of various nuclear processes, a large amount of radionuclides were discharged into aquatic systems. The migration and transfer behavior of radionuclides in the environment depends on the prevailing geochemical conditions and processes influencing the speciation of radionuclides. Sorption on clay minerals strongly influences the fate and mobility of radioactive contaminants in the geosphere. Therefore, understanding the migration behavior of radioactive and non-radioactive toxic substances is essential for a reliable long-term safety assessment of potential nuclear waste disposal sites, and of subsurface dumps and sites with radioactive and/or heavy metal containing inventory. Clay minerals are among the most important sorbents for metal cations in soils and sediments due to the high abundance of clays, their large specific surface area, negative surface charge, and reactive surface hydroxyl groups [1,2].

Humic acid (HA) is a chemically heterogeneous compound having different types of functional groups at different proportions and configurations [3]. HA is organic matter that is defined as the fraction of humic substances soluble at pH values >1. HA solubility increases with increasing pH and decreases with increasing inert electrolyte concentration [4]. HA contains carboxyl (—COOH), hydroxyl (—OH), amine (—$NH_2$), and phenol (Ar—OH) functional groups, and has negative charges in weakly acidic-to-basic media due to deprotonation reactions [5]. It is very important to know the nature of organic functional groups of HA in the process of determining the stability of metal ion complexes. HA may enhance or reduce metal ion sorption, depending on the relative stabilities of metal–HA binary and metal–HA-clay surface ternary complexes as a function of pH [6].

Rectorite is an abundant clay mineral in China. Structure and characteristics of it are similar to those of montmorillonite [7]. It is a kind of regularly interstratified clay mineral with alternate pairs of dioctahedral mica-like layer (nonexpansible) and dioctahdral smectite-like layer (expansible) existing in 1:1 ratio. The cations of $Na^+$, $K^+$ and $Ca^{2+}$ lie in the interlayer region between 2:1 mica-like layers and 2:1 smectite-like layers [8], while the exchangeable hydrated cations reside in the latter. The structure of rectorite can also cleave easily between smectite-like interlayers, forming monolithic rectorite layers (2 nm thick). Because of the presence of smectite layer in rectorite, it is anticipated that surface physicochemical properties of rectorite would be similar to that of smectite. Properties such as a strong sorption capacity, good stability in water and an easy regeneration has led to this material being tested as a sorbent of many cations and anions from the environment [9–13]. However, research on metal ion sorption to rectorite in the presence of HA, which represents a major fraction of dissolved organic compounds present in freshwater, is still scarce [12,13]. A better macroscopic and spectroscopic description of metal ion, HA, and rectorite interactions is still needed to improve the understanding of the behavior of metal ions and HA in the environment.

Removal of long-lived radionuclides from nuclear waste solutions is an important environmental concern in nuclear waste management. In this work, the structures and species of surface

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sorbed/complexed Eu(III) on rectorite in the absence and presence of HA were characterized by using powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and extended X-ray absorption fine structure (EXAFS) spectroscopy. The effect of pH on the sorption of Eu(III) and HA to Na-rectorite was investigated, and the experimental data of Eu(III) sorption in the absence and presence of HA were simulated by the diffuse-layer model (DLM) with the aid of FITEQL 3.2 software. Europium was selected as both a fission product and a homologue of trivalent lanthanides and actinides [14]. Measurements were made, at low metal ion concentration, to get as close as possible to environmental concentration. This paper highlights the potential environmental application of rectorite in the removal of Eu(III) in the presence of HA in environmental pollution cleanup.

## 2. Experimental

### 2.1. Materials

All reagents were of analytical reagent grade and used without further treatment. Milli-Q water was used in all experiments. Eu (III) stock solution at 0.1 mol/L was prepared from $Eu_2O_3$ (Purity, 99.99%) after dissolution, evaporation, and redissolution in 0.001 mol/L perchloric acid. The radiotracer $^{152+154}$Eu(III) was used in the batch sorption experiments. The Na-rectorite sample was derived from Zhongxiang county (Hubei, China). The characterization results of Na-rectorite were reported in earlier reports [13]. In brief, the $N_2$-BET surface area was 11.9 $m^2/g$, and the average particle size was 7.4 μm. The water content of 5.7% was taken into account in the calculation of the Na-rectorite content.

HA was extracted from a soil from Gansu province (China) and was characterized by nuclear magnetic resonance and pyrolysis-capillary gas chromatography electron impact mass spectrometry. HA did not contain any inorganic constituents. The main constituents were the following: C, 60.44%; H, 3.53%; N, 4.22%; O, 31.31%; and S, 0.50% [15].

### 2.2. Characterization

The morphology of samples was obtained with scanning electron microscope (SEM) (JSM-6700F). Selected samples doped with Eu(III) were characterized using FTIR (Perkin Elmer spectrum 100, America) in pressed KBr pellets. For FTIR spectroscopy analysis, the samples were washed 3 times with ethanol for 5 min, filtered, and dried at 343 K for 24 h.

XRD measurements were performed by D/Max-2400 Rigaku X-ray powder diffractometer operated in the reflection mode with Cu Kα ($\lambda = 0.15418$ nm) radiation. XPS data were obtained with a Thermo ESCALAB 250 electron spectrometer from VG Scientific using 150 W Al Kα radiation. EXAFS spectra were measured at beamline U7C of the National Synchrotron Radiation Laboratory (Hefei, China). After sorption experiments, Na-rectorite loading Eu(III) and/or HA was for SEM, FTIR, and XRD measurements. Samples preparation for XPS and EXAFS analysis were conducted using a 500 mL vessel with 0.2 g/L Na-rectorite, 0.01 mol/L $NaClO_4$, and 0.2 μmol/L Eu(III) at pH = 5.0. For HA effect, Na-rectorite and $NaClO_4$ were pre-equilibrated for 24 h, then HA was added to equilibrate for 24 h, and finally, Eu(III) stock solution was added. Detailed processes for the sample preparation for XPS and EXAFS analysis are shown in Supporting information SI 1.

The acid–base titrations of Na-rectorite and HA suspension were carried out by potentiometric titration experiments [16–18], which was conducted in a 100 mL Teflon vessel with a polyethylene lid. The vessel was surrounded with a glass jacket to maintain a temperature of 25.0 ± 0.5 °C. A Teflon bar was used for stirring. All titrations were conducted using a computer controlled PC-titration system (DL50 Automatic Titrator, Mettler Toledo) with pH electrode (Delta 320). Argon was bubbled successively through NaOH, $HClO_4$, and Milli-Q water to exclude $CO_2$(g). Before beginning the titrations, Na-rectorite or HA suspension and background electrolyte were added to the vessel and purged with argon for at least 2 h. The pH was quickly lowered to approximately 3.0 by addition of 1.5721M $HClO_4$. The high concentration of $HClO_4$ could acidify the suspension quickly without obvious changing of solution volume. After 1 h of equilibrium, the suspensions were slowly back-titrated at a variable increment (0.008 up to 0.15 mL, which was automatically adjusted to keep a stable pH change value) with 0.04668M NaOH solution to pH 11. Each step was allowed to stabilize until the pH drift was less than 0.005 pH unit per minute. The low concentration of NaOH assured the gentle change of pH after each titration point. The data sets of pH versus the net consumption of $H^+$ or $OH^-$ in the absence of metal ions due to surface complexation were used to obtain intrinsic acidity constants with the aid of FITEQL 3.2 software.

### 2.3. Sorption experiments

The sorption of Eu(III) on Na-rectorite was investigated by using batch sorption experiments in polyethylene centrifuge tubes sealed with a screw-cap under $N_2$ condition. The stock suspension of Na-rectorite and $NaClO_4$ solution were pre-equilibrated for 24 h, and then, Eu(III) stock solution was added to achieve the desired concentrations of the different components. The system was adjusted to the desired pH by adding negligible volumes of 0.01 or 0.1 mol/L $HClO_4$ or NaOH.

For HA adsorption at different pH values, Na-rectorite and $NaClO_4$ were pre-equilibrated for 24 h, then HA was added, and the pH was adjusted. Samples were gently shaken for 24 h, and then centrifuged for 30 min at 18,000 rpm (Allegra 64R Centrifuge, Beckman Coulter) for the separation of solid phase from aqueous phase, pH was measured, and the concentrations of HA in the supernatants were determined using a UV–vis spectrophotometer (UV-2550, Shimadzu, Kyoto, Japan) at 259.6 nm (calibration at different pH values, and consideration of the contribution of ions leached out from Na-rectorite to the UV–vis signal).

For the effect of HA on Eu(III) sorption, Na-rectorite and $NaClO_4$ were pre-equilibrated for 24 h, then HA was added to equilibrate for 24 h, and finally, Eu(III) stock solution was added to achieve the desired concentrations of different components. Preliminary studies indicated that the sorption of Eu(III) on Na-rectorite achieved equilibrium in several hours. Samples were gently shaken for 24 h to obtain complete sorption equilibrium and then centrifuged for 30 min at 18,000 rpm for the separation of solid phase from aqueous phase. The efficiency of separation was checked by photo-correlation spectroscopy, which showed no colloidal particles in the supernatant solution.

The counting of $^{152+154}$Eu(III) was analyzed by Liquid Scintillation counting using a Packard 3100 TR/AB Liquid Scintillation analyzer (PerkinElmer) with the scintillation cocktail (ULTIMA GOLD AB™, Packard). The sorption percentage $R$ was calculated according to the equation of $R(\%) = 100 \times (1 - A_L/A_{tot})$; herein, $A_{tot}$ is the activity of the suspension and $A_L$ is that of the supernatant.

## 3. Results and discussion

### 3.1. Batch experiments

Fig. 1A shows that HA adsorption on Na-rectorite decreases with increasing pH. HA adsorption is strongly dependent on