



## Effects of dissolved and fixed humic acid on Eu(III)/Yb(III) adsorption on aluminum hydroxide: A batch and spectroscopic study

Zhulin Niu<sup>a</sup>, Toshihiko Ohnuki<sup>b</sup>, Eric Simoni<sup>c</sup>, Qiang Jin<sup>a,d</sup>, Zongyuan Chen<sup>a,d,\*</sup>, Wangsuo Wu<sup>a,d</sup>, Zhijun Guo<sup>a,d,\*</sup>

<sup>a</sup> Radiochemistry Laboratory, School of Nuclear Science and Technology, Lanzhou University, 730000 Lanzhou, PR China

<sup>b</sup> Tokyo Institute of Technology, Inst Innovat Res, Lab Adv Nucl Energy, Meguro Ku, 2-12-1-N1-16 Ookayama, Tokyo 1528550, Japan

<sup>c</sup> Univ Paris Saclay, Univ Paris Sud, CNRS IN2P3, Inst Phys Nucl Orsay, F-91405 Orsay, France

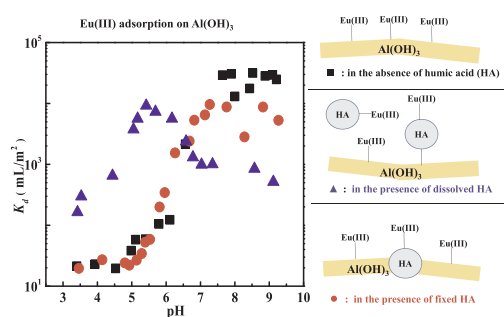
<sup>d</sup> The Key Laboratory of Special Function Materials and Structure Design, Ministry of Education, Lanzhou University, 730000 Lanzhou, PR China



### HIGHLIGHTS

- Both individual and co-transport of U(VI) is controlled by U(VI) concentration.
- AKC exhibits two opposite effects on U(VI) transport depending on U(VI) concentration.
- AKC is more sensitive to the change of pH and *I* after U(VI) adsorbed on it.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

Humic acid (HA) in the environment may exist in either dissolved or fixed forms. However, laboratory studies usually take only the former into account. Here we synthesized a hybrid of HA and aluminum hydroxide (Al(OH)<sub>3</sub>) to mimic fixed HA, compared the effects of fixed and dissolved HA on Eu(III)/Yb(III) adsorption on Al(OH)<sub>3</sub>, and analyzed the adsorption mechanisms using time resolved laser induced fluorescence spectroscopy (TRLFS), X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS). It was found that dissolved HA affected significantly Eu(III)/Yb(III) adsorption on Al(OH)<sub>3</sub>, whereas fixed HA showed little apparent effect on the adsorption. The spectra of TRLFS, XPS and EXAFS for Eu(III)/Yb(III) adsorption on Al(OH)<sub>3</sub> in the presence of dissolved/fixed HA could be reproduced by those for Yb(III)/Eu(III) adsorption in the absence of HA and those for Yb(III)/Eu(III) binding to dissolved HA, respectively. Spectroscopic analyses indicated that the different effects of fixed and dissolved HA on Eu(III)/Yb(III) adsorption were due to different surface speciation with the same surface species, which could be interpreted by the decrease of available sites on fixed HA as compared to those on dissolved HA. This study implied that the effects of HA on the adsorption of Eu(III)/Yb(III) as well as other trivalent lanthanides/actinides in the environment might be overestimated if the differences between dissolved and fixed HA were not considered.

\* Corresponding authors at: Radiochemistry Laboratory, School of Nuclear Science and Technology, Lanzhou University, 730000 Lanzhou, PR China.  
E-mail addresses: [zychen@lzu.edu.cn](mailto:zychen@lzu.edu.cn) (Z. Chen), [guozhj@lzu.edu.cn](mailto:guozhj@lzu.edu.cn) (Z. Guo).

## 1. Introduction

Humic substances (HSs) play a critical role in the migration of heavy metals and radionuclides in the environment. In recent years, concerns about the safety assessment of high-level nuclear waste (HLW) repository have increased efforts to better define the interactions between mineral surfaces and radionuclides in the presence of HSs [1–6]. Fulvic acid (FA) and humic acid (HA) are usually considered as HSs' representatives. Purified HA and FA have been extensively studied with metal ions and mineral surfaces in binary and ternary systems. Advanced models such as NICA-Donnan [7,8], Model VI [9] and Ligand and Charge Distribution (LCD) model [10,11] have been developed to describe interactions between FA/HA and metal ions as well as the adsorption of heavy metal cations in the presence of FA/HA.

In laboratory studies, purified FA/HA are usually added directly into adsorption systems and considered as dissolved species in aqueous phase [12–14]. In the environment, however, HSs co-exist with various minerals and metal cations, with which some parts of HSs are fixed in solids due to flocculation and sedimentation processes. Some functional groups of fixed HA/FA are complexed with mineral surfaces, and the others are occupied by ubiquitous high valent metal cations, such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ . It can be expected that available amounts of functional groups on fixed HA/FA in the environment should be less than that on dissolved HA/FA. Thereby, fixed HA/FA should have different effects on heavy metal adsorption as compared to that of dissolved HA/FA. However, direct evidence from laboratory investigation on this subject is still scarce. To the best of our knowledge, how to assess the effects of fixed HA/FA on the adsorption of heavy metals and radionuclides has been paid little attention. A primary difficulty in carrying out a study with fixed FA/HA is to find a reasonable model system which contains fixed FA/HA and its composition is simple enough to exhibit the effect of fixed FA/HA. Natural organic soils or sediments contain fixed HSs but their complicated composition hampers spectroscopic analyses and further comparison of the differences between fixed and dissolved FA/HA [15].

In this study, two model systems were designed to compare and understand the different effects of fixed and dissolved HA on Eu(III)/Yb(III) adsorption on aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ).  $\text{Al}(\text{OH})_3$  was chosen as a representative mineral because the flocculation of HSs with  $\text{Al}^{3+}$  exists widely in the environment. The first system (HA +  $\text{Al}(\text{OH})_3$ ) was a reference system which included dissolved HA and  $\text{Al}(\text{OH})_3$  suspension. It was used to collect adsorption data in the presence of dissolved HA. The second system (HA@ $\text{Al}(\text{OH})_3$ ) contained a hybrid of HA and  $\text{Al}(\text{OH})_3$ , which was used to mimic a representative mineral (i.e.  $\text{Al}(\text{OH})_3$ ) with fixed HA in the environment. The hybrid was prepared by precipitating a mixed solution of dissolved aluminum nitrate and HA at high pH. Batch experiments were performed to compare the effects of dissolved and fixed HA of same mass amount on Eu(III)/Yb(III) adsorption on  $\text{Al}(\text{OH})_3$ . Measurements of time resolved laser induced fluorescence spectroscopy (TRLFS), X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) were carried out in parallel to follow corresponding mechanisms.

## 2. Experimental

### 2.1. Materials and characterization

Stock solutions of Eu(III)/Yb(III) were prepared by dissolving their high pure oxides (99.99%) in 6 mol/L HCl/ $\text{HNO}_3$  solution. HA (Aldrich) was purified from humic acid sodium salt (Aldrich) according to the protocol suggested by the International Humic Substance Society. HA stock suspension (1 g/L) was prepared by diluting it in NaOH solution (pH  $\approx$  10) in order to completely dissolve purified HA. All other chemicals used were of analytical grade. All solutions and suspensions were prepared with boiled ultra-pure water (18  $\text{M}\Omega\text{ cm}^{-1}$ ).

$\text{Al}(\text{OH})_3$  solid was prepared by  $\text{Al}^{3+}$  hydrolysis and precipitation in

**Table 1**  
Mineralogy and specific surface areas of the adsorbents.

Sample	Description	HA mass content (%)	Mineralogy* of $\text{Al}(\text{OH})_3$ , % content	B.E.T. $\text{m}^2\text{g}^{-1}$
$\text{Al}(\text{OH})_3$	$\text{Al}(\text{OH})_3$	0	Gibbsite 19.4 Bayerite 80.6	9.88
HA25@ $\text{Al}(\text{OH})_3$	Hybrid	2.5	Gibbsite 27.6 Bayerite 71.4	40.9
HA50@ $\text{Al}(\text{OH})_3$	Hybrid	5.0	Gibbsite 33.8 Bayerite 62.6	43.9

\* Mineralogy was obtained by XRD analyses (Fig. S1).

aqueous solution [16,17]. Ammonium hydroxide solution (0.25%) was dropped into hot  $\text{Al}(\text{NO}_3)_3$  solution (0.1 mol/L, 75 °C) under stirring until pH value reached 8.0. The suspension was settled at  $75 \pm 2$  °C for 7 days and then cooled to ambient temperature. The precipitate was purified by dialyzing and then freeze dried. The hybrid of HA and  $\text{Al}(\text{OH})_3$  was prepared with a similar protocol except that HA was added into  $\text{Al}(\text{NO}_3)_3$  solution at pH 5.0 and the mixture was stirred for 5 h before ammonium hydroxide was dropped at 75 °C. The loss of HA during dialysis was negligible according to the TOC analyzing of outside solution.

X-ray powder diffraction (XRD) patterns were recorded using a Rigaku D/max-2400 diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418$  nm). Scanning electron micrographs (SEM) were obtained with a JEOL JSM-5600LV scanning microscope. B.E.T. areas were calculated from the nitrogen adsorption/desorption isotherms at 77 K using a Micrometrics ASAP 2010 surface analyzer.

### 2.2. Batch experiments

Batch-type adsorption experiments were carried out in centrifuge tubes at  $T = 22 \pm 2$  °C. An appropriate amount of adsorbent was dispersed in NaCl solution (0.1 mol/L). The desired pH values of suspensions were achieved by adjusting with dilute NaOH or HCl solutions. Radiotracer  $^{152+154}\text{Eu}(\text{III})$  was added with stable Eu(III). After Eu(III)/Yb(III) with or without HA were added into the suspensions, the samples were shaken for 3 days. Preliminary kinetic experiments indicated that a 3-day contact time was sufficient to reach adsorption equilibrium. After the final pH value of suspension was measured, the solid and liquid phases were separated by centrifugation (12,000 rpm, 30 min). Eu(III) concentration in the supernatant was measured by liquid scintillation counting (Tri-Carb 3110TR LSC, PerkinElmer, USA), whereas Yb(III) concentration was measured by ICP-MS (Perkin-Elmer Elan-6000). The data exceeding three times of Yb(III) detection limit (500 ppt) were taken into account. The analytical precision was around 1%.  $^{133}\text{Cs}$  was used as internal standards to correct instrumental instabilities. The distribution coefficients of Eu(III)/Yb(III) ( $K_d$ ,  $\text{mL/m}^2$ ) were calculated by the following equation:

$$K_d = \frac{C_0 - C_{eq}}{C_{eq}} \frac{V}{m \cdot \text{B.E.T.}}$$

where  $C_0$  and  $C_{eq}$  were initial and final concentrations in the aqueous phase, respectively;  $m$  the solid mass;  $V$  the liquid volume; and B.E.T. the specific surface area.

### 2.3. TRLFS

The concentrations of Eu(III), HA and  $\text{Al}(\text{OH})_3$  were  $1 \times 10^{-4}$  mol/L, 25 mg/L and 0.5 g/L, respectively. The suspensions for TRLFS analysis were prepared under  $\text{N}_2$  atmosphere. Several suspensions at different pH values were shaken for 3 days to reach Eu(III) adsorption equilibrium, transferred into cuvettes, sealed and used for TRLFS. The

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