Microscopic insights into the temperature-dependent adsorption of Eu(III) onto titanate nanotubes studied by FTIR, XPS, XAFS and batch technique

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HIGHLIGHTS

► Eu(III) interaction is promoted at higher temperature.
► Eu(III) interaction is a spontaneous and endothermic process.
► Eu(III) interaction is controlled by outer-sphere surface complexation at low T.
► Eu(III) interaction is controlled by inner-sphere surface complexation at high T.
► The results are important to understand Eu(III) physicochemical behavior.

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ABSTRACT

This work investigated the effects of reaction temperature on Eu(III) interaction mechanism and microstructure at the titanate nanotubes (TNTs)/water interface by batch and spectroscopic (FTIR, XPS, XAFS) technique. Batch adsorption results showed that the adsorption of Eu(III) onto TNTs is promoted at higher temperature, and is an endothermic and spontaneous interfacial process. The adsorption isotherms at three different temperatures can be described by the Freundlich model better than the Langmuir model did. The spectroscopic analysis results suggested that Eu(III) interaction with TNTs is mainly controlled by outer-sphere surface complexation at $T = 293$ K, which is a reversible adsorption process, whereas Eu(III) interaction is mainly controlled by inner-sphere surface complexation at $T = 313$ K and $T = 343$ K, which is an irreversible adsorption process. The findings in this work can help us to better understand the physicochemical behavior of Eu(III) and related radionuclides in natural environment. The results of this work also show the great potential importance of TNTs as novel nanomaterials in the near future of nuclear waste management.

1. Introduction

Recently, the interfacial behavior and effective remediation of lanthanides and actinides have received increased attention in nuclear waste management [1–4]. In order to study the interfacial behavior of lanthanides and actinides and their potential pollution towards the natural water and soil environment, the understanding of interaction mechanism and microstructure of lanthanides and actinides at the solid/water interface are of great importance [1–3]. Eu(III), which is a trivalent lanthanide and also a chemical homologue to trivalent actinides, has been widely used as a model element to study the interaction mechanism and microstructure of lanthanides and actinides at solid/water interface due to the similar interfacial behavior between Eu(III) and other lanthanides and actinides [3–5]. Therefore, the interaction mechanism and microstructure of Eu(III) at the solid/water interface have been extensively studied largely based on various macroscopic and spectroscopic measurement methods [1–7]. The results indicated that Eu(III) interaction is generally affected by solution pH, while is more or less dependent on ionic strength, and the microstructure mainly includes the formation of outer-sphere or inner-sphere surface complexes depending on solution chemistry [6,7].

Since their discovery by Kasuga et al. [8,9], titanate nanotubes (TNTs) have come under intense multidisciplinary studies due to their one-dimensional nanostructure, excellent physiochemical property and versatile applications such as solar cells, catalyst supports, photocatalysis, sensors, novel adsorbents and electrolumi-

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nescent hybrid devices [8–10]. In recent years, the adsorption behavior of TNTs to various environmental contaminants including organic dyes [11,12], heavy metal ions [13–16] and radionuclides [7] have been widely investigated. For example, Lee and co-workers [11,12] used TNTs for the removal of organic dyes from aqueous solutions. Liu et al. [13] studied the adsorption behavior of Cu(II) onto TNTs by using batch technique. Chen et al. [14] studied the adsorption behavior of Pb(II) onto TNTs. The removal of Eu(III) and Ni(II) onto TNTs by adsorption process was investigated in our previous reports [7,15]. All of these investigations indicated that TNTs are promising adsorbents for the potential application in the environmental contaminants removal from wastewater treatment. However, these studies mainly focused on the macroscopic adsorption kinetics and thermodynamics of environmental contaminants onto TNTs largely based on batch technique, little attention has been paid to the interaction mechanism and microstructure of environmental contaminants at the TNTs/water interface at molecular level [7]. In our previous report, the interaction mechanism and microstructure of Eu(III) onto TNTs as a function of contact time, solution pH, humic acid (HA) and fulvic acid (FA) was studied by batch and EXAFS technique at molecular level [7].

In addition, it is well known that temperature is an important water quality parameter in the natural environment. In various environmental compartments, temperature can fluctuate diurnally, seasonally, spatially, affecting the adsorption, microstructure, fate and transport of environmental contaminants in natural soil and water [17,18]. Thereby, it is quite necessary to study the temperature effect on the interaction mechanism and microstructure of environmental contaminants at the solid/water interface [18,19]. However, few studies with respect to the temperature effect on interaction mechanism and microstructure are available [18–20]. Sheng et al. [18] found that the growth of surface coprecipitates is favored at higher temperature for Ni(II) uptake on diatomite. Yang et al. [20] observed a trend from outer-sphere surface complexation at low temperature to inner-sphere surface complexation at high temperature for Ni(II) uptake on mordenite surfaces.

Herein, the microscopic insights into the temperature-dependent adsorption of Eu(III) onto TNTs was studied. The main objective of this work was to evaluate the effect of temperature on the interaction mechanism and microstructure of Eu(III) onto TNTs using a combination of batch, Fourier Transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) measurements. This paper highlights that the variation of temperature can greatly change the interaction mechanism and microstructure governing the fate and transport of trace Eu(III) in heterogeneous aquatic environments.

2. Materials and methods

2.1. Materials and chemicals

Eu(III) stock solution was prepared from Eu_2O_3 after dissolution, evaporation and redissolution in 10^{-3} mol/L $HClO_4$. All the other chemicals studied in our experiments were purchased of analytical purity and had been used without any further purification. Milli-Q water was used to prepare all the solutions in our experiments.

TNTs were prepared by a simple hydrothermal process from TiO_2 particles which is similar to that described by Kasuga et al. [3,4] and had been characterized in detail in our previous report [7]. In brief, 3 g TiO_2 particles was first mixed with 90 mL 10 mol/L NaOH solutions, and then the mixture was treated for 24 h at 150 °C in a 250 mL Teflon-lined autoclave by a simple hydrothermal process. After that, the formed precipitate was

washed with 0.1 mol/L HCl solution and distilled water respectively until the rinsing solution pH is close to 7.0, and then the precipitate was separated by a filtration process. The as-prepared samples were dried at 120 °C for 8 h in a vacuum oven and stored in a glass bottle. The tube structures of ~10 nm in outer diameter and hundreds nanometers in length can be clearly observed from the scanning electron microscope (SEM) and transmission electron microscopy (TEM) images (Fig. 1) of TNTs [7]. The layer structure of mostly 3-fold can be recognized. No particulate structure of TiO_2 precursor was found in every view field, indicating that whole TiO_2 was converted to TNTs by hydrothermal synthesis. Compared with carbon nanotubes, TNTs were less adhesive to each other; the tube ends were released and kept open [7]. Inductively coupled plasma mass spectrometry (ICP-MS) analysis showed that TNTs contained Na atoms of ~0.15 wt% [7]. The X-ray Diffraction (XRD) pattern (Fig. S1) of the as-prepared TNTs agrees well with that appears in references, where the indices were determined based on the calculation for a scrolled titanate nanosheet ($H_2Ti_3O_7$). All the observed XRD peaks (2 theta ≈ 10°, 25°, 29° and 50°) were assigned to TNTs, and the intense peak at about 10° was attributed to interlayer space of TNTs [7]. As it can be seen from the Fourier transform infrared (FTIR) spectrum (Fig. S2) of the as-prepared TNT samples, a broad and intense band located at about 3200 cm^{-1} is attributed to the O–H stretching mode, indicat-
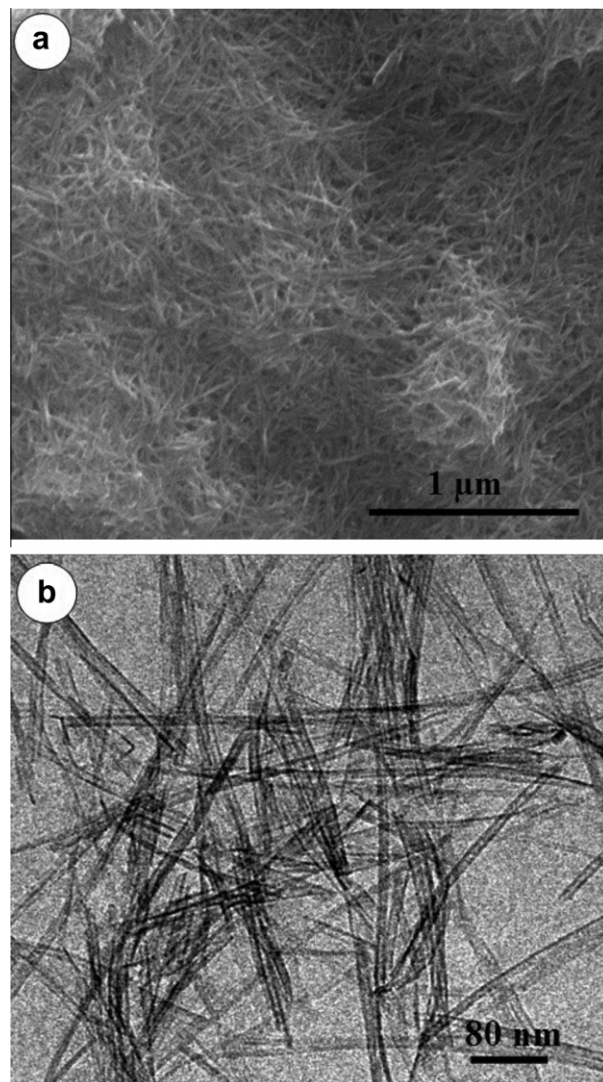

Fig. 1. SEM (a) and TEM images (b) of the as-prepared TNT samples [7].