



Macroscopic and spectral exploration on the removal performance of pristine and phytic acid-decorated titanate nanotubes towards Eu(III)



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ABSTRACT

In the present work, the titanate nanotubes (TNTs) were synthesized via the hydrothermal approach and the phytic acid decorated TNTs (PA/TNTs) were prepared by using the one-pot method. Batch technique was adopted to explore the removal performance of TNTs and PA/TNTs towards Eu(III) under various environmental conditions. At pH 4.0 and 5.5, the sorption of Eu(III) on TNTs decreased with increasing NaNO₃ concentration, while the removal of Eu(III) by PA/TNTs was independent of ionic strength. The saturated Eu(III) sorption capacities of TNTs and PA/TNTs were calculated to be 9.52×10^{-4} and 9.57×10^{-4} mol/g at pH 5.5 and 298 K, being higher than a variety of previously reported adsorbents. PA/TNTs also exhibited high selectivity for capturing Eu(III) from a simulated wastewater containing multiple competing metal ions. According to the Fourier transform infrared spectroscopy (FTIR), solid fluorescence and X-ray photoelectron spectroscopy (XPS) analysis, the predominant removal mechanisms of TNTs and PA/TNTs towards Eu(III) at pH 5.5 were ion exchange/outer-sphere surface complexation and inner-sphere surface complexation, respectively. These experimental findings demonstrated the wide application prospects of TNTs and PA/TNTs for the highly efficient purification of Eu(III)-bearing wastewater.

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1. Introduction

Extensive growth of nuclear activities induces the leakage of various radionuclides (e.g. ²³⁵U, ⁶⁰Co, ¹⁵²⁺¹⁵⁴Eu, ²³⁵Np, ²³⁹Pu, ²⁴¹Am, ²⁴⁴Cm, etc.) into the soil and water environment [1]. Specifically, ¹⁵²⁺¹⁵⁴Eu and the trivalent minor actinides (e.g. ²⁴¹Am, ²⁴⁴Cm) possess similar chemical properties and comparable environmental behaviors [2,3]. Owing to their chemical and radiological toxicity, ¹⁵²⁺¹⁵⁴Eu, ²⁴¹Am and ²⁴⁴Cm may pose severe damages to the biosphere and human beings [4,5]. Hence, it is urgent to remove these trivalent lanthanides/actinides from the aquatic systems.

Sorption approach is widely used in the disposal of radionuclide-bearing wastewater due to its multiple superiorities of easy operation, low cost, high availability and favorable removal performance [6–8]. Natural minerals (e.g. hydroxyl magnesium silicate (HMS) [1], kaolinite [9] and natural red earth (NRE) [10] with abundant sources and low cost) and carbon nanomaterials (e.g. multi-walled carbon nanotubes (MWCNTs) [11], carbon nanofibers (CNFs) [12] and graphene oxide

(GO) nanosheets [13] with large surface area and high stability) have been adopted as potential adsorbents for the removal of Eu(III). In addition, researchers have also decorated a series of organic ligands onto the surfaces of these solid materials and synthesized new composites with higher Eu(III) sorption capacities [3,14–20]. However, it is worth noting that the capabilities of these adsorbents for selectively capturing Eu(III) are still not satisfied. Besides, the sequestration mechanisms of Eu(III) have not been clearly identified by using the spectroscopic analysis. Therefore, the design of advanced materials with low synthesis cost, favorable removal performance, excellent selectivity and explicit structure-property relationship are of great necessity.

TNTs, a kind of Ti-based nanomaterial with typical tubular morphology, have been widely applied in the elimination of toxic metal ions and organic pollutants [21–25]. In our previous study [26], the phytic acid (PA) molecules were decorated onto the TNTs surfaces via the one-pot procedure. Specifically, this inositol hexaphosphate was used as the functionalized ligand due to its low toxicity, abundant phosphate groups and strong complexing ability for heavy metal ions. The as-prepared PA/TNTs with plentiful phosphate sites showed higher sorption capacity and favorable selectivity for U(VI). Considering the high affinity between lanthanides and phosphate groups [27–29], the PA/TNTs composite is expected to possess high effectiveness for Eu(III) enrichment. In view of this, batch experiments were performed under different

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environmental conditions to evaluate the sorption trends of Eu(III) on PA/TNTs and pure TNTs (for comparison). In addition, the underlying removal mechanisms were further clarified on the foundation of batch experimental results and spectroscopic evidences (e.g. FTIR, solid fluorescence and XPS).

2. Experimental

2.1. Chemical reagents

The TiO₂ powder (as precursor to fabricate TNTs) was purchased from *Adamas Reagent, Ltd.* PA in analytic pure was obtained from *Toronto Research Chemicals Inc.* Eu(NO₃)₃·6H₂O was purchased from *Shanghai Energy Chemical Co., Ltd.* All other chemical reagents were purchased in analytical purity and directly used without further purification. The Eu(III) stock solution was prepared by dissolving a quantified amount of Eu(NO₃)₃·6H₂O into the Milli-Q water.

2.2. Preparation and characterization of adsorbents

The TNTs and PA/TNTs samples were prepared by using the methods as reported in our previous work [26]. The XPS spectra of these two materials were collected by using a Kratos Axis Ultra DLD spectrometer with a monochromatic Al K α X-ray source (1486.6 eV). Specifically, the analysis chamber pressure was $<5.0 \times 10^{-9}$ Torr. The pass energy values of 160 eV and 40 eV were used for collecting the survey and narrow scan spectra, separately.

2.3. Macroscopic sorption experiments

The batch experiments of Eu(III) sorption on TNTs and PA/TNTs were conducted under ambient conditions. Briefly, a certain volumes of adsorbent suspension, NaNO₃ and Eu(III) stock solution were

synchronously added into the centrifuge tubes. Herein, sodium nitrate was used as the background electrolyte due to the widespread presence of Na⁺ and NO₃⁻ ions in the natural and contaminated aquatic environment. A specific concentration of 0.01 mol/L was selected to simulate the common ionic strength in most of the water systems [30–32]. The pH values were adjusted by adding a tiny amount of diluted (0.1 or 0.01 mol/L) HNO₃/NaOH solutions. Note that the deviation for the solid/liquid ratios of the used adsorbents (herein, TNTs and PA/TNTs) is $<1\%$ due to the pH adjustment. Afterwards, the polyethylene tubes were gently oscillated for a contact time of 24 h and the suspensions were centrifuged at 9000 rpm for 10 min. The supernatant was then taken out and filtered with 0.22- μ m filtration membrane. The concentration of Eu(III) in the filtrates was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The sorption percentage ($S, \%$) and sorption capacity ($q_e, \text{mol/g}$) were calculated by using the Eqs. (1) and (2) as follows:

$$S = (C_0 - C_e) / C_0 \times 100\% \quad (1)$$

$$q_e = (C_0 - C_e) \cdot V / m \quad (2)$$

Herein, C_0 (mol/L) and C_e (mol/L) are the initial and equilibrium concentrations of Eu(III) in solution, respectively. The parameter m/V (g/L) is the solid-to-liquid ratio of the sorption systems.

2.4. Spectra collection of pristine and sorption samples

The samples for spectral analysis were prepared by adopting an approach similar to that used in the batch experiments. The FTIR spectra of adsorbents before and after Eu(III) sorption were recorded on a Thermo Nicolet 6700 spectrometer within the wavelength range of 4000–400 cm⁻¹. The solid fluorescence spectra of standard (Eu(NO₃)₃·6H₂O and EuPO₄·H₂O(s)) and sorption samples were collected with a Craic

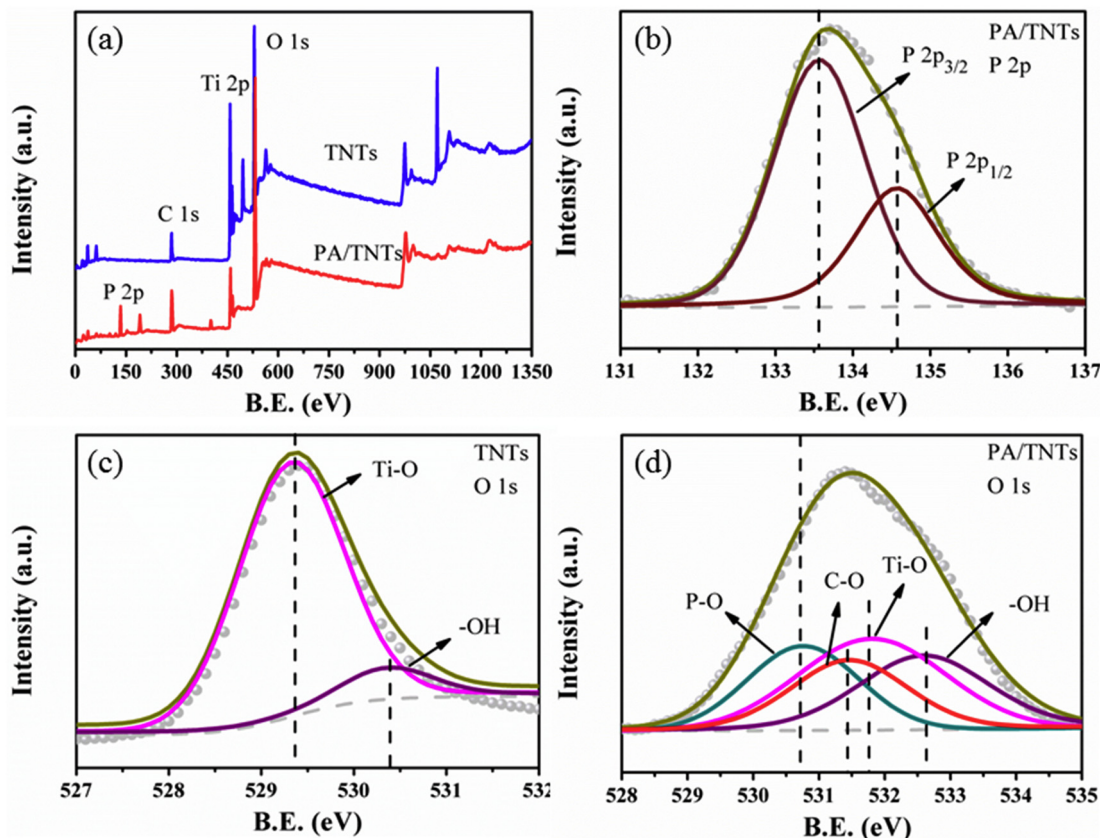


Fig. 1. XPS survey scans of TNTs and PA/TNTs (a); High-resolution P 2p spectrum of PA/TNTs (b); High-resolution O 1s spectra of TNTs (c) and PA/TNTs (d).

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