Original Research

Efficient adsorption of europium (III) and uranium (VI) by titanate nanorings: Insights into radioactive metal species

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Radioactive wastewater containing high concentration of radionuclides poses severe threats to ecosystem and human health, so efficient removal of these toxic heavy metals is urgently needed. Titanate nanomaterials have been demonstrated good adsorbents for heavy metals due to ion exchange property. In this study, titanate nanorings (TNRs) were synthesized using the facile hydrothermal-cooling method. The TNRs were composed of sodium trititanate, with a chemical formula of Na0.66H1.34Ti3O7·0.27H2O and a Na content of 2.38 mmol/g. The TNRs demonstrated sufficient adsorption performance to radionuclides europium (Eu) and uranium (U) ions. Specifically, even at a high initial concentration of 50 mg/L, 86.5% and 92.6% of the two metal ions can be rapidly adsorbed by the TNRs within 5 min, and equilibrium was reached within 60 min at pH 5. The maximum adsorption capacity (Qmax) obtained by the Langmuir isotherm model was 115.3 mg/g for Eu(III) and 282.5 mg/g for uranium (U(VI)) at pH 5, respectively. The adsorption capacities of the two metals under various water chemical conditions were highly related to their species. Ion exchange between metal cations and Na+ in the TNR interlayers was the dominant adsorption mechanism, and adsorption of U(VI) was more complicated because of the co-existence of various uranyl (UO22+) and uranyl-hydroxyl species. The spent TNRs were effectively regenerated through an acid-base or ethylenediamine tetraacetic acid (EDTA) treatment and reused. Considering the large adsorption capacity and quick kinetic, TNRs are promising materials to remove radionuclides in environmental purification applications, especially emergent treatment of leaked radionuclides.

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1. Introduction

Titanate nanomaterials (TNMs) derived from TiO2 have attracted increasing interest for research in recent years due to their specific characteristics [1–4]. Distinct from TiO2, which is a widely used photocatalyst, TNMs exhibit distinguished physicochemical properties, including a large specific surface area, sufficient ion exchange performance, and abundant surface functional groups (—OH/—ONa) [1–4]. Therefore, TNMs are considered to be suitable adsorbents for various cations, including cationic dyes [5,6], ionic organic pollutants [7,8], metals [9–11], and radionuclides [12,13]. A hydrothermal reaction is generally applied to fabricate TNMs [1,14], and titanate-based nanomaterials with various morphologies have been reported, including titanate nanotubes (TNTs) [13,15,16], titanate nanofibers [13], titanate nanosheets [17,18], titanate nanoribbons [19], and titanate nanowires [20,21].

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As long-living radionuclides, lanthanides and actinides are of great concern as they pose serious risks to aquatic ecosystems and human health given their high toxicity and carcinogenicity. Adsorption using functional materials has been confirmed as an efficient technique for radionuclide removal from waters [22–25]. Understanding the interfacial behaviors and underlying mechanisms of lanthanides and actinides at the materials/water interface is important for the long-term assessment of nuclear and radioactive waste repositories. Europium (Eu) is typically utilized as a homologue of trivalent lanthanides and actinides because of its similar physicochemical properties [26]. Uranium (U) is a radionuclide and a commonly used nuclear material, and 238U is the most abundant isotope [27]. U(VI), predominately existing as UO2²⁻, is more soluble and mobile than U(IV) [28], and thus the transport and transformation of U(VI) are greatly affected by water chemical conditions such as pH, co-existing conventional ions, and dissolved organic matter [29–31]. Therefore, studying the removal of U(VI) under various conditions is necessary. Nuclear leakage accidents such as the Chernobyl nuclear accident and the Fukushima nuclear accident usually cause high concentrations of radionuclides poured into natural aquatic environment.

TNMs have demonstrated high adsorption capacities for Eu(III) and U(VI) because of their sufficient ion exchange properties. For example, the efficient uptake of Eu(III) by TTNs was because of their abundant functional groups, large surface areas, and specific crystal structures [32–34]. TNMs are generally composed of edge-sharing [TiO₆]₃ units as the basic skeleton and Na⁺/H⁺ locating in the lattice interlayers, so the interlayered Na⁺/H⁺ are exchangeable sites which can be easily replaced by metals cations like Eu³⁺ [32–34]. Both sodium and hydrogen titanate exhibited high U(VI)/adsorption capacities [12,35,36], even under complicated water chemical conditions. However, titanate with various structures and compositions will offer different adsorption properties for metals, but deep insights into metal adsorption capacity and mechanisms related to both TNM characteristics and metal physicochemical parameters are still needed to be investigated. In this study, as a new TNM member, titanate nanorings (TNRs) were also postulated to also possess high adsorption capabilities for radionuclides. In addition, the facile synthesis of TNRs can reduce fabrication costs and expand practical application. However, no information is currently available on the synthesis of TNRs and their corresponding application for heavy metals removal. Moreover, the adsorption mechanisms of radionuclides by TNRs should also be explored. Compared with the previously reported TNMs (e.g., TTNs) for heavy metals adsorption, this study further gave the new insights into: 1) the adsorption mechanism of radionuclides with different species by TNRs, 2) the reason why ring-like titanate could be formed through a facile hydrothermal process, and 3) adsorption behaviors of typical radionuclides under various water chemistry conditions. The presented findings can promote a better understanding of heavy metals adsorption by TNM with specific structure and composition for practical application.

In this study, a facile hydrothermal-cooling method was developed to fabricate titanate nanorings for the first time, which were then used to remove Eu(III) and U(VI) from waters via adsorption. Industrial wastewater level Eu(III) and U(VI) concentrations (50 mg/L in a typical adsorption experiment) are considered. A series of batch experiments were conducted that aimed to: 1) develop a novel hydrothermal-cooling method to synthesize and characterize the ring-like titanate nanomaterials; 2) explore the effectiveness of TNRs for Eu(III) and U(VI) adsorptive removal through adsorption kinetics and isotherms; 3) investigate the influences of pH, co-existing ions, and humic acid (HA) on adsorption; 4) elucidate the adsorption mechanisms based on specific TNR structures and compositions; and 5) evaluate the reusability of TNRs. This study not only focuses on the interaction mechanisms between material-radionuclides interfaces but is also valuable for practical applications of TNRs and radionuclide removal from contaminated water.

2. Materials and methods

2.1. Synthesis of TNRs

The chemicals used in this study are presented in Text S1 of the supplementary data. The TNRs were synthesized via a hydrothermal-cooling method that was modified from the widely used alkaline hydrothermal method [5,14,37]. First, 0.3 g of nano-anatase powder was dispersed in 67 mL of NaOH solution (~15 M, BDH, USA) through microwave digestion [37]. TNR characterization was carried out according to previous studies [9], including the investigation on morphology, crystal phase, elemental composition, oxidation state, Brunauer-Emmett-Teller (BET) specific surface area, pore volume, average pore diameter, and zeta potential. Details of the material characterization are shown in Text S2 of the supplementary data.

2.2. Batch adsorption tests

Batch experiments were conducted in polyethylene bottles (50 mL in total volume) in duplicate, where the adsorption of Eu(III) and U(VI) in the bottles was excluded in the blank tests. For the adsorption kinetics tests, 0.025 g of TNRs were added to the metal solution (50 mL), and the initial Eu(III) and U(VI) concentrations were prepared at 50 mg/L and a pH of 5. Adsorption proceeded by shaking the solutions at 200 rpm and a temperature of 25 ± 0.5 °C for 3 h, and samples were taken at designed times for further measurement. Adsorption isotherm tests were carried out with initial Eu(III) and U(VI) concentrations ranging from 10 to 100 mg/L, and 0.5 g/L of TNRs with a pH of 5 was added, and adsorption lasted for 3 h. The pH was adjusted to 2–10 to investigate its effect on adsorption. The concentration of inorganic Na⁺ and Ca²⁺ in the chloride form was 0.5–10 mM to test the effect of co-existing ions. In addition, 10 mM K⁺ (in the chloride form), HCO₃⁻ and H₂PO₄⁻ (in the sodium form) were also added at pH 5 to test the effect of various co-existing ions on adsorption respectively. HA concentration varied from 0 to 10 mg/L in terms of total organic carbon (TOC) to test the natural organic matter effect. Eu(III) and U(VI) species as a function of pH were determined using the software MEDUSA.

After adsorption, the suspension was filtered through a cellulose acetate membrane with a pore size of 0.22 μm. Concentrations of Eu(III) and U(VI) in the supernatant were determined using inductively coupled plasma-optical emission spectrometer (710-ES, Varian, USA). The adsorption capacities (q, mg/g) and removal efficiencies (R, %) of Eu(III) and U(VI) at equilibrium are calculated as:

\[ q_t = \frac{(C_0 - C_f)V}{m} \]  

(1)
\[ R = \frac{(C_0 - C_e)}{C_0} \times 100\% \]

where \( q_t \) (mg/g) is the adsorption capacity of metal ions at time \( t \) (min), \( C_0 \) and \( C_e \) (mg/L) are the initial and equilibrium concentrations of metal ions, respectively, \( V \) (L) is the total volume of the solution, and \( m \) (g) is the mass of the TNRs.

2.3. Metals desorption and TNR regeneration

An acid–base procedure was performed to desorb metals and regenerate TNRs [38]. After Eu(III) or U(VI) (\( C_0 = 50 \) mg/L) was adsorbed onto the TNRs (0.5 g/L) with a pH of 5, the material was filtered and then immersed into a 0.2 M HNO\(_3\) solution by stirring for 3 h for metal ion desorption. Afterwards, the material was separated and immediately immersed into 0.2 M of NaOH for 3 h for TNR regeneration. For comparison, 0.2 M of ethylenediamine tetraacetic acid (EDTA) was also applied to desorb metals and regenerate TNRs. The adsorption and regeneration cycle was repeated five times.

3. Results and discussion

3.1. Characterizations of TNRs

Transmission electron microscopy (TEM) images of TiO\(_2\) (nano-anatase) and TNRs are shown in Fig. 1. The TiO\(_2\) precursors exhibit spherical particles with an average diameter of ~50 nm (Fig. 1a). After the hydrothermal treatment for TNR synthesis, the nanoparticles completely transformed into ring-like nanomaterials (Fig. 1b). High-resolution TEM (HRTEM) further revealed that the synthesized TNRs are multilayered (10–20 layers) and that each nanoring is a closed circle (Fig. 1c). This morphology of TNRs is extremely different from that of the TNTs obtained in previous studies, which presented as open-ended nanotubes with 3–5 layers [5,9]. In addition, the spacing lattice distance TNRs is 0.78 nm (Fig. 1c), which is affiliated with the titanate (020) crystal plane [14,39]. An energy dispersive spectra (EDS) analysis suggested that the primary elements of TNRs were Ti, O, and Na, in accordance with the composition of sodium titanate [38].

The X-Ray diffraction (XRD) patterns of the TiO\(_2\) and TNRs before and after metal adsorption are illustrated in Fig. 2. For TiO\(_2\), all the peaks belong to anatase (JCPDS 21–1272) [40]. For TNRs, the peaks with 2\( \theta \) at ca. 10°, 24°, 28°, 48°, and 62° are classified as sodium trititanate, with a postulated chemical structure of Na\(_x\)H\(_{2-x}\)Ti\(_3\)O\(_7\) (\( x = 0–0.75 \) depending on the interlayered sodium content) [9,15]. The diffraction at 9.48° indicates the interlayer...
distance of the TNRs, as marked at 0.78 nm in the HRTEM image (Fig. 1c). For the specific titanianate structure, triple edge-sharing [TiO₆] octahedrons compose the layers as the primary TNR skeleton, and Na⁺/H⁺ is located in the interlayers as the exchangeable sites [9,11,15,41]. With Eu(III) and U(VI) adsorbed, the crystalline structure of TNRs was nearly unchanged, which is probably because ion exchange occurred in the interlayers but did not change the basic [TiO₆] skeleton, as this is always the dominant mechanism of the adsorption of metal cations by sodium TNMs [9,11,15,42]. However, the interlayer peak at 9.48° shifted to 9.28° for TNRs-Eu and 9.10° for TNRs-U. The lower 2θ degree suggests an expanded interlayer distance between TNRs after adsorption, resulting from the replacement of Na⁺ by metal cations with a larger radius (i.e., Eu³⁺ and UO₂²⁺ in this study) [9,11].

TNRs exhibit similar crystalline phases but different morphologies compared with TNTs. Hypothetically, if we use a nano-scissor to cut off a nano-ring section and then can straighten this broken ring, we find that the nano-ring turns into a nanotube. Therefore, TNRs can be recognized as an end-to-end TNTs, and the hydrothermal-cooling method is the key procedure for the formation of rings but not tubes. TiO₂ transforms into trititanate during the hydrothermal process (at 180°C for 3 h), while the subsequent cooling treatment facilitates ring formation. This is because TNMs tend to form a more stable structure that quickly reduces the total energy when the temperature drastically decreases. The loop-ended structure of TNR is a more stable form compared with tubular structure, and a quick loss of system energy (i.e., dramatical decrease in temperature in this study) leads to the formation of ring-like material [14,15,20,43]. Compared with the hydrothermal conditions for TNTs synthesis (e.g., 140 °C or 150 °C for 24 h, 130 °C for 72 h, 200 °C for 30 h, etc.) [10,11,14,15,33], the preparation of TNRs in this study only took 1 h at a slightly higher temperature (180 °C), which greatly reduced the energy costs. More importantly, TNRs may have more stable structures compared to TNTs with a large length–diameter ratio; hence, the new materials cannot be easily damaged at the nanoscale, which is important for material reuse [38].

The BET surface area of TNRs reached 202.5 m²/g, which is much larger than that of the precursor TiO₂ (45.1 m²/g) (Table S1). The TNRs also exhibited a large pore volume of 0.94 m³/g. Clearly, type IV adsorption–desorption isotherms were observed for TNRs, and they also exhibited H3 type desorption hysteresis loops according to the Brunauer-Deming-Deming-Teller (BDDT) classification (Fig. S1a), indicating that mesopores with diameters ranging from 2 nm to 50 nm were present in the TNRs [44]. Pore size profiles of the TNRs displayed a bimodal distribution (Fig. S1b). The pores centered at 3–4 nm belong to the inner diameter of the hollow rings, while the larger pores at 10–20 nm are the diameter of an entire ring and the voids between different rings [45–47]. After hydrothermal treatment, the point of zero charge (pH ZP) of anatase (6.1) dramatically decreased to 2.7 for the TNRs. The large surface area and low pH ZP of the TNRs may facilitate its efficient adsorption of metal cations.

### 3.2. Adsorption kinetics and isotherms

In the adsorption kinetics profiles (Fig. 3a), it is clear that the adsorption process was extremely quick for both Eu(III) and U(VI) by TNRs, as high removal efficiency rates of 86.5% for Eu(III) and 92.6% for U(VI) were achieved within 5 min. When adsorption reached equilibrium at 60 min, the removal efficiencies of Eu(III) and U(VI) were 98.1% and 99.9%, respectively, demonstrating the
prominent adsorption performance of the material.

Pseudo-first order and pseudo-second order kinetic models were employed to interpret the adsorption process, as illustrated in Eqs. (3) and (4) [48–50]:

\[
q_t = q_e - q_e \exp(-k_1t)
\]

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

where \(q_t\) and \(q_e\) (mg/g) represent the metal adsorption capacity at time \(t\) (min) and equilibrium, respectively. \(k_1\) (min\(^{-1}\)) and \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) are the corresponding rate constants.

As the fitting parameters suggest (Table S2), the kinetic results fit the pseudo-second order model better for the adsorption of both Eu(III) and U(VI), as high correlation coefficients approaching 1.00 (\(R^2 \geq 0.9999\)) were obtained. In addition, the simulated \(q_e\) values from the model are very close to those obtained from the batch experiments (relative deviation <1%). This indicates that the chemical interaction between metal ions and TNRs is likely the rate-controlling step, occurring as the metal ions first diffuse from the liquid onto the TNR surface through electrostatic attraction and then react with –OH groups [9,49]. Therefore, the large BET surface area and abundant functional groups of TNRs plays a significant role in the rapid adsorption of Eu(III) and U(VI).

For the adsorption isotherm results analysis (Fig. Sb), the Langmuir (Eq. (5)) and Freundlich (Eq. (6)) isotherm models were employed to simulate the experimental data [51,52]:

\[
q_e = \frac{Q_{\text{max}}bC_e}{1 + bC_e}
\]

\[
q_e = K_F C_e^{1/n}
\]

where \(b\) is the Langmuir constant (L/mg) representing adsorption energy, \(K_F\) ((mg/g)/(L/mg))\(^{1/n}\) is the Freundlich capacity constant, and \(n\) is the heterogeneity factor.

Table S3 lists the parameters for adsorption isotherm models after fitting. The Langmuir model better simulated the isotherm data (\(R^2 > 0.998\)), indicating that the monolayer adsorption of the metal ions onto the TNR surfaces dominated the removal mechanism [51]. The maximum adsorption capacity (\(Q_{\text{max}}\)) was 115.3 mg/g (0.76 mmol/g) for Eu(III) and 282.5 mg/g (1.19 mmol/g) for U(VI) at a pH of 5 and temperature of 25 °C. Therefore, TNRs have excellent adsorption performance for the two metals, which was far superior to that of most conventional adsorbents listed in Table S4, such as activated carbon, TiO\(_2\), nano-magnetite, and natural minerals [31,53–56].

Previous researches have also evaluated the adsorption performance of TNTs for Eu(III) and U(VI), the most widely studied TNMs. Interestingly, the adsorption capacity of Eu(III) by TNRs was much larger than the 18.7 mg/g adsorption capacity achieved by TNTs at a pH of 4.5 and a temperature of 20 °C [33,34]. The U(VI) adsorption capacity is only slightly lower than that by sodium TNTs (333 mg/g at a pH of 5.0 and temperature of 25 °C) reported in our previous work [12] but is much higher than that of hydrogen TNTs (17.6 mg/g at a pH of 5.0 and temperature of 20 °C) as reported by Yuan et al. [35]. Generally, the crystal phases of precursor TiO\(_2\), hydrothermal conditions (including NaOH concentration, hydrothermal time, and temperature), and washing procedure all affect the structure and composition of formed TNMs [1,20,37,57,58]. Previously, a systematic study was conducted to investigate the key factors that dominated the adsorption capacity of metal cations, and it suggested that the Na content in TNMs played a primary role [37].

Therefore, ion exchange between metal cations and interlayered Na\(^+\) determined the adsorption capacity [9,37,59]. The TNT synthesis procedure in the work of Sheng et al. contained an acid washing procedure, thus leading to a low Na content (0.065 mmol/g), causing the composition of TNs to be more closed to hydrogen titanate (H\(_2\)Ti\(_3\)O\(_7\)) and thus exhibiting low adsorption capacity of Eu(III) [33,34]. This also explains the low U(VI) adsorption capacity by hydrogen titanate in the study by Yuan et al. [35]. However, the TNTs synthesized in our previous work possessing a high Na content of 3.33 mmol/g resulted in a high U(VI) adsorption capacity [12]. Consequently, the Na content of the TNs at 2.38 mmol/g based on an X-ray photoelectron spectroscopy (XPS) analysis (see Section 3.5), which was close to that of sodium trititanate, determined the large adsorption capacity of metal cations. Therefore, compared with the conventional TNs, TNs show advantages on adsorptive removal of radioactive cations such as Eu(III) and U(VI): firstly, TNs can be fabricated through a facile hydrothermal method with obviously reduced reaction time, thus leading to decrease in energy conservation and low cost; secondly, high Na content in TNs implies good adsorption performance for the radionuclides; thirdly, loop-locked structure indicates a more stable structure than TNs and low Ti leaching during adsorption, which was confirmed by the material reuse test in Section 3.6.

3.3. Influence of pH on Eu(III) and U(VI) adsorption by TNRs

Fig. 4 presents the variation in adsorption capacity as the pH ranges from 2 to 10, and Fig. S3 plots the metal species distribution at various pH. The uptake of the two metal ions were both weak under a strong acidic condition (pH 2) with a low \(q_e\) of 17.2 mg/g and 31.4 mg/g for Eu(III) and U(VI) respectively, as the TNs were positively charged (Fig. S2) and cannot efficiently capture the metal cations (Eu\(^{3+}\) and UO\(_2\)\(^{2+}\)) due to the electrostatic repulsion (Fig. S3). At a pH of 3, the \(q_e\) of Eu(III) and U(VI) sharply increased to 58.0 mg/g and 73.1 mg/g, respectively, because the surface charge of the TNs became negative, thus facilitating the capture of metal cations through electrostatic attraction. A further increase in pH from 3 to 5 led to gradually increasing \(q_e\) due to more negative charges being carried on the TNR surfaces (Fig. S2). The optimum pH for adsorption was observed at 5–6, where the \(q_e\) value reached 98.1 mg/g for Eu(III) and 99.9 mg/g for U(VI) at a pH of 5.
Interestingly, a further increase in pH from 6 to 8 and above led to different adsorption behaviors for the two metals, as precipitation occurred at weak alkaline conditions while metal anions formed at higher pH (Fig. S3). For Eu(III) adsorption at a pH of 6–8, the primary species were Eu(OH)\(^+\), EuOH\(^2+\), and Eu(OH)\(^3+\) (Fig. S3); therefore, the TNRs could still efficiently adsorb these metal cations through ion exchange. However, the precipitation of Eu(OH)\(_3\) formed at pH \(\geq 8\) and metal anions Eu(OH)\(^-\) dominated the species when pH > 9, resulting in a decrease in the adsorption capacity when pH > 8. For example, \(q_e\) at a pH of 9 (70.3 mg/g) was lower than that at a pH of 9 (90.1 mg/g). U(VI) adsorption is more complicated with an increase in pH because various U(VI) species form (Fig. S3).

Table S5 presents the aqueous reactions of UO\(_2^+\) [12,30]. TNRs can effectively adsorb U(VI) cations at a pH of 5–6, mainly UO\(_2^+\), (UO\(_2\))\(_2\)((OH)\(^7\), (UO\(_2\))\(_3\)(OH)\(_5\), and (UO\(_2\))\(_4\)(OH)\(_7\). However, at a pH of 7–8, the co-precipitation of U(VI) in the form of insoluble UO\(_2\)(OH)\(_2\) with TNRs was the dominant mechanism [59]. A dramatic decrease in the \(q_e\) of U(VI) was found when the pH increased from 8 to 10, as U(VI) were mainly presented as anions of (UO\(_2\))\(_3\)(OH)\(_5\) and (UO\(_2\))\(_4\)(OH)\(_7\) in this pH range (Fig. S3), which cannot be captured well by the negatively charged TNRs.

### 3.4. Effects of co-existing ions and HA on Eu(III) and U(VI) adsorption by TNRs

Fig. 5a displays the effects of frequently co-existing metal ions on adsorption. Generally, Na\(^+\) only showed a minor inhibitive effect, and the \(q_e\) decreased by 5.1% for Eu(III) and 3.4% for U(VI), with the Na\(^+\) concentration increasing from 0 to 10 mM, respectively. It is because Na\(^+\) in the interlayers of lattice is the exchange site and exogenous Na\(^+\) only affected the aggregation of TNRs [60]. The inhibitive effect of Ca\(^+\) was more obvious; \(q_e\) decreased from 98.1 mg/g to 81.7 mg/g (by 16.7%) for Eu(III) and from 99.9 to 65.1 mg/g (by 34.8%) for U(VI) as the Ca\(^+\) concentration increased from 0 to 10 mM, respectively. It is widely reported that the effect of inhibition mechanisms caused by inorganic ions on metal adsorption by TNMs include: (1) competition against target ions on adsorption sites and (2) the enhanced aggregation of materials due to their higher ionic strength [9,61]. The divalent Ca\(^+\) with lower hydration energy and hard-soft acid-base (HSAB) hardness is more competitive than Na\(^+\) in the adsorption process [61–64], leading to a stronger electrostatic double-layer compression effect and a more severe aggregation of TNRs [60,61]. Moreover, it is noteworthy that the inhibition of U(VI) adsorption caused by Ca\(^+\) was more complicated due to the formation of UC\(^+\)-CO\(_3\)\(^-\) complexes, as shown in Eqs. (7) and (8) [12,65]. TNRs cannot capture these anionic and electro-neutral complexes well, leading to a clear decrease in the adsorption capacity in the presence of Ca\(^+\).

\[
\begin{align*}
\text{UO}_2^{2+} + \text{Ca}^{2+} + 3\text{CO}_3^{-} & = \text{CaUO}_2(\text{CO}_3)_3^{2-} \\
\text{UO}_2^{2+} + 2\text{Ca}^{2+} + 3\text{CO}_3^{-} & = \text{Ca}_3\text{UO}_2(\text{CO}_3)_3^{(aq)}
\end{align*}
\] (7) \quad (8)

Fig. S4 further summarizes the effects of different co-existing ions on adsorption of Eu(III) and U(VI) at pH 5. It is found that, all the inorganic ions with high concentration (10 mM) inhibited the two metals adsorption. Specifically, similar to Na\(^+\), K\(^+\) also slightly inhibited the adsorption of Eu(III) and U(VI), mainly due to the competition for adsorption sites [9]. Cl\(^-\) showed negligible effect and this effect could be attributed to Na\(^+\) as NaCl was added. Carbonate and bicarbonate showed adverse effect adsorption, especially for U(VI), and the \(q_e\) decreased from 98.9 to 60.0 mg/g (by 39.9%) for U(VI). CO\(_3\)\(^-\)/HCO\(_3\) can easily bind with U(VI) to form anionic complexes, thus inhibiting adsorption [30]. H\(_2\)PO\(_4\) had more inhibition effect on Eu(III) adsorption, as the \(q_e\) decreased from 98.1 to 69.1 mg/g (by 29.6%). The series of phosphate species are strong ligands that can complex with metals, leading to the formation of anionic complexes and low adsorption capacity [66,67].

Fig. 5b shows the effect of HA on adsorption. Generally, HA may pose a two-sided influence on metals adsorption. On the one hand, HA can bind metal ions to form soluble metal-HA complexes, such as the binary complexes EuHA(III) and UO\(_2\)HA(II), and ternary complexes of EuOH/HA(II) and UO\(_2\)(OH)HA(I) [31,34], which were much more difficult to capture than free metal cations by TNMs from the solution. On the other hand, HA molecules can also be adsorbed onto TNTs, and the sorbed HA can further bind with more metals ions through surface complexation, which enhances the apparent adsorption capacity [12,34,60]. In this study, increased Eu(III) and U(VI) adsorptions with a higher HA dosage were observed, suggesting that the further capture of metal ions by TNMs-sorbed HA played a dominant role. Fig. S5 further confirmed the higher adsorption of HA onto TNRs with an increasing HA concentration, with a distribution coefficient \((K_d)\) of 6.0 L/g. Specifically, the \(q_e\) of Eu(III) increased from 98.1 to 123.0 mg/g, while the \(q_e\) of U(VI) increased from 99.9 to 115.3 mg/g, respectively. The
promotion effects caused by HA are consistent with previous results. Sheng et al. claimed that co-existing HA could enhance Eu(III) adsorption by TNTs at pH < 6 due to its outer-sphere surface complexation and the formation of Eu-bridging ternary surface complexes (HA/FA-Eu-TNTs) [34]. Our previous work also found the promoted adsorption of U(VI) by TNTs because of the complexation of UO$_2^{2+}$ with sorbed HA [12,68]. In addition, the coating of HA onto TNMs could inhibit aggregation of the material due to steric hindrance effect [60], which also facilitated adsorption because of sufficient interaction between metal ions and active sites.

3.5. Adsorption mechanisms

To clearly explore the adsorption mechanism, the chemical composition of the TNRs before and after adsorption were further analyzed using XPS (Fig. 6). As listed in Table S6, the element composition analysis revealed that the TNR elements are Ti (27.44%), O (66.52%), and Na (6.04%), which is in agreement with the EDS results (Fig. 1d). According to the basic structure of trititanate [9,15], the chemical composition of the synthesized TNRs is expressed as Na$_{0.66}$H$_{1.34}$Ti$_3$O$_7$•0.27H$_2$O, and the obtained sodium content (2.38 mmol/g) is consistent with the value obtained through the acid dissolution method.

After the adsorption of Eu(III) and U(VI), the Na 1s peak was greatly reduced, and Eu 3d and U 4f peaks appeared (Fig. 6a), again suggesting that the interlayered Na$^+$ was exchanged by the heavy metal cations during adsorption. Moreover, Na$^+$ in the interlayer of TNRs played the dominant role compared with H$^+$, and —ONa was the primary ion exchange site, while —OH contributed minor to metals adsorption [11,37,59]. Based on the determined Eu (1.54%) and U (1.97%) contents and unchanged trititanate skeleton, the TNR compositions after adsorption can be expressed as Na$_{0.27}$H$_{0.25}$Ti$_3$O$_7$•0.34H$_2$O and Na$_{0.17}$H$_{1.64}$(UO$_2$)$_{0.22}$(OH)$_{0.25}$Ti$_3$O$_7$•0.27H$_2$O, respectively. At a pH of 5, Eu(III) is the primary species adsorbed onto the TNRs (Fig. S3). However, the proposed two different methods to reuse TNMs, i.e., conventional acid and EDTA treatments. TNRs can be effectively

Fig. 6. (a) XPS survey and (b) high resolution of O 1s spectra for TNRs before and after metals adsorption.
regenerated and repeatedly used for Eu(III) and U(VI) removal (Fig. 8), as the removal efficiency of the two metals in the fifth cycle was still as high as 91.7% and 90.6% after HNO₃—NaOH treatment and 93.2% and 93.9% after EDTA regeneration, respectively. An acid—base desorption-regeneration procedure was applied so as to efficiently desorb the metal ions and also restore the adsorption sites [38]. During the acid—base process, H⁺ with an extremely high concentration firstly replaces the interlayered metal ions, while the tubular structure may be broken due to the high acidic condition [38, 74]. Further NaOH treatment can restore not only the Na⁺ sites but also the tubular structure. As a strong complexing agent, EDTA can bond metal ions and lead to desorption from TNRs. In addition, sodium EDTA used in this study can also restore the Na⁺ sites of TNRs, resulting in a sufficient TNR reuse property. In addition, the stability of TNRs during five Eu(III) desorption-regeneration cycles was evaluated. Table S7 shows only 4.06 wt% and 1.07 wt% of Ti were leached after the 5th cycle upon acid-base and EDTA procedure, indicating good stability of the material in the application for metal adsorptive removal.

4. Conclusions

In summary, the novel titanate nanorings demonstrated sufficient adsorption performance for Eu(III) and U(VI), realizing monolayer maximum adsorption capacities of 115.3 and 282.5 mg/g, respectively, according to the Langmuir isotherm model. In addition, the two metals were rapidly adsorbed by TNRs, as 86.5% of Eu(III) and 92.6% of U(VI) with an initial concentration of 50 mg/L can be removed within 5 min. Ion exchange in the interlayers was the dominant adsorption mechanism, and the high Na content (2.38 mmol/g) in the TNRs led to its large metal adsorption capacity. The adsorption behaviors and capacities of the two metals under different water chemical conditions were highly related to their species in the solution. Various uranyl cation, anion, and molecule formations led to a complicated adsorption of U(VI), while Eu³⁺ ion exchange was the main mechanism for Eu(III) adsorption. Spent TNRs can be efficiently regenerated without obvious adsorption capacity loss via an acid—base or EDTA treatment. Considering the quick kinetics, high adsorption capacity, and sufficient reusability, TNRs are promising materials for the removal and recovery of radionuclides from wastewaters, and the TNRs have great applications for emergency treatment of leaked radionuclides.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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