



New insights into Th(IV) speciation on sepiolite: Evidence for EXAFS and modeling investigation



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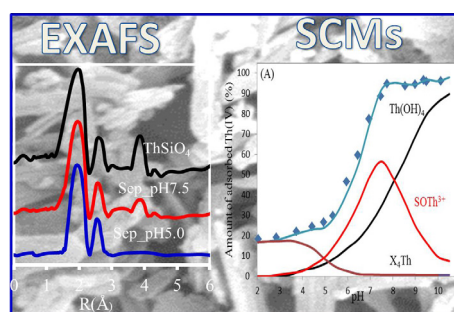
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HIGHLIGHTS

- No effect of ionic strength on Th(IV) removal was observed at pH >5.0.
- Th(IV) sorption on sepiolite at pH 7.5 was surface precipitation by EXAFS analysis.
- Th(IV) sorption can be satisfactorily fitted by surface complexation modeling.

GRAPHICAL ABSTRACT



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ABSTRACT

The interaction mechanism of Th(IV) on sepiolite was investigated by batch, EXAFS and surface complexation modeling. The batch experiments revealed that the sorption of Th(IV) on sepiolite remarkably decreased with increasing of ionic strength at pH <5.0, while no effect of ionic strength on Th(IV) removal was observed at pH >5.0. The removal kinetics and isotherms of Th(IV) on sepiolite can be satisfactorily simulated by the pseudo-second-order and Langmuir model, respectively. The analysis of EXAFS spectra for sepiolite-Th(IV) at pH 5.0 and 7.5 indicated that the sorption of Th(IV) on sepiolite at pH 5.0 and 7.5 was inner-sphere surface complexation and surface precipitation, respectively. The results of surface complexation modeling showed that Th(IV) sorption on sepiolite can be fitted by a cation exchange sites (X_4Th species) at pH <4.5, an inner-sphere surface complexation ($SOTH^{3+}$ species) at near neutral and a surface precipitation at pH >7.0 very well. These findings are crucial for the evaluation of fate and transport of Th(IV) at water-mineral interface.

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1. Introduction

The pollution of radionuclides paid the increasing attention in recent years due to their potential threat to publics, especially after the Fukushima accident in 2011 [1,2]. Therefore, it is mandatory to remove radionuclides below the allowable concentration range. So far, the removal of radionuclides on a variety of adsorbents has been recently studied such as synthetic materials [3–6], metal

(hydr)oxides [7–11] and clay minerals [12–15]. Among these adsorbents, clay minerals have been extensively used due to the effective capacity, low-cost, easy operation and environmentally friendly. Sepiolite ($\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_6(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$, as a typical clay mineral) has been employed to remove various heavy metals due to its micro-fibrous structure and high surface area [16–20]. Sun et al. found that the maximum adsorption capacity of sepiolite calculated from Langmuir model were 22.85 and 18.47 mg/g for Eu (III) and U(VI), respectively [21]. To the authors' knowledge, investigation concerning the sorption of Th(IV) on sepiolite is still scarce nowadays [22].

Recently, the interaction mechanism of radionuclides at water-solid interface have been extensively investigated using extended X-ray absorption fine structure (EXAFS) spectroscopy [23–32] and surface complexation modeling (SCM) [26,33–37]. Sun et al. based on the EXAFS spectra analysis demonstrated that the sorption of U(VI) on sepiolite displayed the U-Si/Al shell at high pH condition, which indicated that the inner-sphere surface complexation were coordinated on SiO_4 tetrahedra via bidentate configuration [21]. Huang et al. found that the sorption of U(VI) on sepiolite can be satisfactorily simulated by diffuse double layer model (DDLDM) with cation exchange site (XNa) at low pH conditions and surface complexation site (SOH) at high pH conditions [38]. However, few studies regarding the removal mechanism of Th (IV) on sepiolite by EXAFS and modeling techniques were available.

The objectives of this study are (1) to elucidate the effect of water chemistry (reaction time, pH, ionic strength, temperature, concentration) on Th(IV) removal by sepiolite by macroscopic experiments; (2) to determine the local structure of Th(IV) on sepiolite at different pH conditions by EXAFS analysis; (3) to simulate the removal of Th(IV) on sepiolite by surface complexation modeling. This manuscript give insight into the fate and transport of Th (IV) at water-mineral interface.

2. Experimental section

2.1. Materials

The sample of sepiolite obtained from Lujiang (Anhui, China) was purified with 0.5 mol/L acetate acid overnight. The stock Th (IV) solution was prepared by dissolving ThO_2 (purity $\geq 99.99\%$) into the concentration HNO_3 solutions. Other chemicals of analytical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Characterization

The morphology of sepiolite was illustrated by SEM (FEI-JSM 6320F). The surface functional groups were characterized by FT-IR (PerkinElmer Spectrum 100 Fourier transform infrared spectrometer, USA) in pressed KBr pellets. The mineralogy of sepiolite was identified by X-ray powder diffraction (XRD, Scintag GLP-10195/07-S, Japan). The chemical states of sepiolite were carried out using XPS (ESCALAB 250 electron spectrometer) with multidection analyzer using Al $K\alpha$ X-ray source (1486.6 eV). The energies of samples were calibrated by C 1 s band at 284.6 eV as a standard. The Nova 4200e instruments (Quantachrome, Boynton Beach, FL, USA) was used to measure the N_2 -BET specific surface area of sepiolite. The zeta potentials of sepiolite at different pH conditions were measured by Malvern Zetasizer Nano ZS.

2.3. Batch adsorption experiments

The triple experiments of adsorption of Th(IV) on the sepiolite were performed at polyethylene tubes under ambient conditions.

The protocol were briefly described as following: suspension of sepiolite and Th(IV) solutions ($m/v = 2.0 \text{ g/L}$) with 0.01 mol/L NaNO_3 solution were added into 10 mL polycarbonate tubes under stirring conditions. The values pH was adjusted by adding negligible volume 0.01–1.0 mol/L HClO_4 or NaOH solution. After equilibrium, the solid phases were separated from liquid phases by centrifugation at 7500 rpm for 10 min. The blank experiments were also performed to minimize the effect of the sorption on the tube walls. The concentration of Th(IV) in supernatant were measured by inductively coupled plasma-mass spectra (ICP-MS). The adsorption percentage (Adsorption, %) and adsorption capacity (Q_e , mg/g) can be calculated the difference between the initial and equilibrated concentration.

2.4. EXAFS analysis

The samples of EXAFS analysis of Th(IV)-containing sepiolite at pH 5.0 and 7.5 were prepared in ambient conditions. Typically, the 0.1 g sepiolite with 0.01 mol/L NaNO_3 were added into 50 mL polycarbonate tubes and then Milli-Q water was added and pre-equilibrated for 24 h. The Th(IV) solutions (5.0 mg/L) were slowly dropwise added under vigorous stirring conditions. Then the suspensions were adjusted to pH 5.0 or 7.5 by using negligible volume 0.01–1.0 mol/L HClO_4 or NaOH solution. Samples were then gently agitated on a shaker for 24 h. The solid phase was separated from liquid phase by centrifugation at 7500 rpm for 20 min and then through 0.22- μm membrane filters. The wet pastes of Th(IV)-containing sepiolite were mounted in Teflon sample holders with Kapton tape. Thorium L_{III} -edge EXAFS spectra were carried out at Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China) using Si(111) double-crystal monochromator. All samples were collected in fluorescence mode with 64-element solid-state Ge detector. The k^2 -weighted EXAFS data were analyzed using Athena and Artemis interfaces to IFFEFIT 7.0 software [39]. The fitting of paths (i.e., Th-O, Th-Si) were obtained from the crystal structure of thorite (ThSiO_4) [40].

2.5. Surface complexation modeling

The sorption of Th(IV) on sepiolite under different pH conditions was fitted by non-electrostatic model with an aid of Visual MINTEQ 3.0 code [41]. The protonation and deprotonation constants can be optimized by Eqs. (1) and (2):



where SOH refers to the amphoteric functional groups of sepiolite. The $\log K_1$ and $\log K_2$ values can be obtained by fitting the potentiometric data of sepiolite at 0.01 mol/L NaNO_3 solution.

3. Results and discussion

3.1. Characterization

The morphology of sepiolite was characterized by SEM image. As shown in Fig. 1A, sepiolite displayed disorder fibrous structures with talc-like ribbons parallel to the fiber axis [21]. It is noted that the gray-like substance on the surface sepiolite was demonstrated to O, Si and Ca elements by Energy Dispersive X-ray Detector analysis (data not shown), which could be attributed to the quartz and calcite/dolomite purity. Fig. 1B shows the FT-IR spectra of sepiolite. The bands at 475 and 682 cm^{-1} could be ascribed to the bending vibration of Si-O-Si in tetrahedral sheet and Mg-OH in Mg_3OH groups, respectively [42]. The band at 1025 cm^{-1} was attributed

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