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Mechanical investigation of U(VI) on pyrrhotite by batch, EXAFS and modeling techniques

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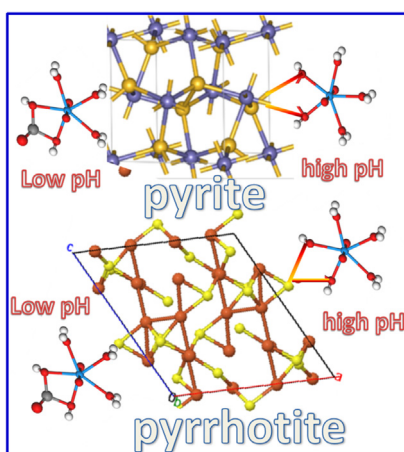
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HIGHLIGHTS

- U(VI) was primarily adsorbed on pyrrhotite and partially reduced by Fe²⁺ and S²⁻.
- XAS demonstrated reductive co-precipitates of U(VI) on pyrrhotite after 168 h.
- Inner-surface complexation dominated the U(VI) removal at pH > 5 by SCMs.

GRAPHICAL ABSTRACT



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ABSTRACT

The interaction mechanism of U(VI) on pyrrhotite was demonstrated by batch, spectroscopic and modeling techniques. Pyrite was selected as control group in this study. The removal of U(VI) on pyrite and pyrrhotite significantly decreased with increasing ionic strength from 0.001 to 0.1 mol/L at pH 2.0–6.0, whereas the no effect of ionic strength was observed at pH > 6.0. The maximum removal capacity of U(VI) on pyrite and pyrrhotite calculated from Langmuir model was 10.20 and 21.34 mg g⁻¹ at pH 4.0 and 333 K, respectively. The XPS analysis indicated the U(VI) was primarily adsorbed on pyrrhotite and pyrite and then approximately 15.5 and 9.8% of U(VI) were reduced to U(IV) by pyrrhotite and pyrite after 20 days, respectively. Based on the XANES analysis, the adsorption edge of uranium-containing pyrrhotite located between U^{IV}O₂(s) and U^{VI}O₂²⁺ spectra. The EXAFS analysis demonstrated the inner-sphere surface complexation of U(VI) on pyrrhotite due to the occurrence of U-S shell, whereas the U-U shell revealed the reductive co-precipitates of U(VI) on pyrrhotite/pyrite with increasing reaction times. The surface complexation modeling showed that outer- and inner-surface complexation dominated the U(VI) removal at pH < 4 and pH > 5.0, respectively. The findings presented herein play a crucial role in the removal of radionuclides on iron sulfide in environmental cleanup applications.

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1. Introduction

The safe disposal and treatment of radioactive wastes produced from nuclear-related industries are a high-priority global environmental issue [1,2]. Uranium (U(VI), as UO_2^{2+} ions) presents high solubility in aqueous solutions, which strongly affects its reactivity and mobility in sub-aqueous environments. Therefore, it is mandatory to remove U(VI) under the allowed emission concentrations (i.e., EPA's MCL is $20 \mu\text{g/L}$ of U and a MCLG of $0 \mu\text{g/L}$ in drinking water) before uranium-containing wastewater discharge into the environment [3–5]. Recently, the removal of U(VI) on various adsorbents has been extensively investigated such as clay minerals [6–8], nanomaterials [9–12], metal (hydr)oxides [13–19] and iron sulphide [20–23]. Pyrrhotite (Fe_{1-x}S , $0 < x < 0.125$) as an iron sulfide mineral is a nonstoichiometric variant of FeS [24,25]. Owing to the weakly magnetic and high redox potential, pyrrhotite has recently been used as a promising adsorbent to remove a variety of environmental constants such as Cu(II) [26], Pb(II) [27], Hg(II) [28,29] and Cr(VI) [30,31]. Cruz et al. found that the reactivity of pyrrhotite was controlled by the formation of oxidation product layers that coated and passivated the pyrrhotite surface [32]. To the authors knowledge, the few studies on the removal of U(VI) on pyrrhotite are available [33].

A variety of spectroscopic techniques (e.g., X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), Extended X-ray absorption fine structure (EXAFS)) [34–40] and surface complexation modeling [2,7,41–44] have been widely used to demonstrate the adsorption and redox of radionuclides at various water-mineral interfaces. Sun et al. used XANES and EXAFS techniques to demonstrate that U(VI) was primitively adsorbed on nanoscale zerovalent iron and then was reduced to U(IV) by Fe^{2+} dissolved from zerovalent iron [45]. However, few investigations towards the interaction mechanism of radionuclides on pyrrhotite and pyrite using the spectroscopic and modeling techniques have been reported.

The objectives of this study are to (1) synthesize and characterize pyrrhotite by using SEM, XRD, FT-IR and XPS; (2) investigate the effect of water chemistries (reaction time, pH, ionic strength, initial concentration and temperature) on removal of U(VI) on pyrrhotite and pyrite by batch technique; (3) determine the interaction mechanism between U(VI) and pyrrhotite and pyrite by using XPS, XANES and EXAFS analysis; (4) simulate the removal of U(VI) on pyrrhotite and pyrite using surface complexation modeling. The results are helpful to understand the application of iron sulfide minerals in nuclear waste management and to evaluate the physicochemical behavior of hexavalent actinides in the natural environment.

2. Experimental

2.1. Synthesis and characterization of pyrrhotite

Pyrrhotite was synthesized by the calcinations of pyrite (obtained from Lujiang Mine in Anhui Province, China) at 650°C for 1.5 h in a N_2 atmosphere [27]. Firstly of all, natural pyrite was finely crushed and sieved to 0.45–0.90 mm using a laboratory mill. The pyrite was purified by soaking it with 10% HCl for 2 h and then washed with Milli-Q water for 4 times. Then, the purified pyrite was placed into quartz glass tube under N_2 atmosphere at 650°C for 1.5 h. As summarized in Table S1 in Supplementary material, the main chemical compositions were Fe 53.63%, S 40.42%, Si 2.42%, O 2.01% and other trace elements such as Mg 0.32%, Cu 0.25%, Ca 0.19% and Al 0.10%, which was comparable with the previous study [46]. The morphology of pyrrhotite was characterized by SEM (FE-SEM, Sirion 200), whereas the identifications of pyrrhotite were recorded by XRD (Dandonghaoyuan 2700, Cu target, electric ten-

sion of 40 kV, electric current of 30 mA, scan rate of $4^\circ/\text{min}$). The zeta potentials of pyrite and pyrrhotite were recorded by using Zetasizer NanoZS (Malvern Instruments). The U(VI) stock solution at $1.0 \times 10^{-3} \text{ mol/L}$ was prepared from $\text{UO}_2(\text{NO}_3)_2$ (spectrographic purity) after dissolution and dilution within $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ solution. Other chemicals were used in this study directly without the further purification.

2.2. Removal experiments

Removal experiments were conducted at anaerobic box under N_2 conditions at 293 K in the presence of $0.001\text{--}0.01 \text{ mol L}^{-1} \text{ NaCl}$. The selected range of ionic strengths is comparable to what is found in the natural setting during the removal of U(VI). Briefly, 0.8 g L^{-1} pyrrhotite/pyrite and 10 mg L^{-1} U(VI) solutions was dropwise added into 10 mL polycarbonate tubes in order to avoid the formation of uranium precipitates, and then the values of pH of suspension were adjusted to be in the range 2.0–10.0 by adding negligible volume of $0.01\text{--}1.0 \text{ mol/L}$ HCl or NaOH solution. The suspensions were shaken for 96 h, which was demonstrated to adequate for the suspension to obtain sorption equilibrium by the preliminary experiments. The solid phases were separated from liquid phases by centrifugation at 9500 rpm for 10 min, and then the supernatant was filtered through a $0.22\text{-}\mu\text{m}$ membrane. The concentration of U(VI) in aqueous solutions was measured by a kinetic phosphorescence analyzer (KPA-11, Richland, USA). The removal percentage of U(VI) (adsorption (%)) and adsorption capacity (Q_s , mg g^{-1}) can be expressed as Eqns. (1) and (2), respectively:

$$\text{Adsorption (\%)} = \frac{(C_0 - C_{\text{eq}}) \times 100\%}{C_0} \quad (1)$$

$$Q_s = \frac{V \times (C_0 - C_{\text{eq}})}{m} \quad (2)$$

where C_0 (mg L^{-1}) and C_{eq} (mg L^{-1}) are initial concentration and concentration after reaction, respectively. m (g) and V (mL) are the mass of pyrite/pyrrhotite and the volume of the suspension, respectively. All experimental data were the average of triplicate determinations and the relative errors were within $\pm 5\%$.

2.3. Analysis of XPS and EXAFS data

The surface functional groups of pyrrhotite were determined by XPS (Thermo Escalab 250 electron spectrometer) using 150 W Al-K α radiations. The XPS spectra were recorded in the constant-pass energy mode at 20 eV with step size of 0.2 eV for the C 1s, Fe 2p, S 2p and U 4f photoelectron lines. All binding energies (BEs) were corrected by calibration on the graphitic carbon C 1s peak at BE 284.6 eV. The energy scale of C 1s was 280–300 eV, 10 sweeps with count time 50 s/step. Uranium L_{III} -edge EXAFS spectra were measured at Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China) using Si(111) double-crystal monochromator. The spectra of all samples were collected in fluorescence mode with high-throughput 30-element solid-state Ge detector. EXAFS spectra were extracted from the subtraction of background and the correction of energy for raw EXAFS data. The k^2 -weighted EXAFS data were analyzed using Athena and Artemis interfaces to IFFEFIT 7.0 software [47]. The fitting of paths (i.e., U-O $_{\text{ax}}$, U-O $_{\text{eq}}$, U-Fe and U-U) was generated from the crystal structures of deliensite ($\text{FeUO}_2(\text{SO}_4)_2(\text{OH})_2(\text{H}_2\text{O})_7$) [48]. The quantitative information on the sample speciation is obtained by a linear combination fit (LCF) of XANES spectra with an aid of IFEFFIT package [49]. The more details regarding the preparation and analysis of EXAFS were provided in the Supporting information (SI).

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