



Reductive immobilization of pertechnetate in soil and groundwater using synthetic pyrite nanoparticles



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HIGHLIGHTS

- First study on reductive immobilization of Tc(VI) using synthetic pyrite particles.
- Synthetic FeS₂ particles effectively reduce and immobilize TcO₄⁻ in water and soil.
- Fe(II) ions on FeS₂ surface are the primary e-donor for reducing Tc(VII) to Tc(IV).
- pH, iron concentration and DOM significantly affect the Tc(VII) reduction rate.
- Synthetic FeS₂ particles may serve as an effective PRB material for Tc-laden water.

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ABSTRACT

Radioactive technetium (⁹⁹Tc) is of intense concern because of its toxicity and high mobility in the environment. Reduction of Tc(VII) to Tc(IV) decreases the mobility and availability of technetium in soil and groundwater. In this study, pyrite nanoparticles (FeS₂) were synthesized, characterized and tested for immobilizing/removing ⁹⁹Tc(VII) in soil and groundwater through batch and column experiments. Influences of particle dosage, dissolved organic matter (DOM), and pH on the reductive immobilization kinetics were examined. At a dosage of 0.28 g/L as Fe, the pyrite nanoparticles were able to rapidly and completely remove 4.88×10^{-7} M of Tc(VII) by converting it to insoluble Tc(IV), with a retarded first-order rate constant of 0.30 h⁻¹. The presence of high concentrations of DOM only moderately inhibited the reduction effectiveness, and acidic pH was more favorable for Tc(VII) reduction. Column experiments showed that embedding a 0.8 cm pyrite layer of the material in a soil bed, simulating a permeable reactive barrier, was able to retard technetium transport 710 times more than a model sandy soil. The results demonstrated that the pyrite particles may serve as a long-lasting reactive material to remediate Tc-contaminated soil, groundwater and solid wastes.

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1. Introduction

Over the past 50 years, about 4.9×10^6 TBq of radioactive wastes have been produced through production and application of fission materials, and the waste pile keeps growing as more nuclear fueled power plants are built (Farrell et al., 1999; Hu et al., 2008).

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Technetium-99 (⁹⁹Tc) is produced in large quantities as a fission product during irradiation of ²³⁵U-enriched fuel for commercial power production and plutonium genesis for nuclear weapons (Um et al., 2011). With a high fission yield of ~6%, ⁹⁹Tc represents the largest fraction of the total long-lived radiation emissions of nuclear wastes (Bruggeman et al., 2007; Um et al., 2011). ⁹⁹Tc has a half-life of 2.13×10^5 years and a specific activity of 650 MBq g⁻¹, and it decays by emitting β⁻-particles with an E_{max} of 300 keV (Wharton et al., 2000; Liu et al., 2008). ⁹⁹Tc accumulated during the treatment of spent nuclear fuels is typically disposed of in geological repositories (Frank et al., 2007). Tc(VII) is often released

into the environment from nuclear weapons testing and low- or intermediate-level nuclear waste disposal (Wharton et al., 2000). In addition, ^{99}Tc can also result from the decay of the medical radioisotope Tc-99m, though it has a much shorter half-life (6.0 h) (Liang et al., 1996).

The solubility, toxicity, sorption and transport behaviors of Tc are often controlled by its speciation and valence state (Peretyazhko et al., 2008a,b). Fig. S1 in the Supporting Information (SI) presents the E_h -pH plot showing the predominant Tc species as a function of redox potential and solution pH. The most prevalent species of dissolved Tc in the environment are Tc(VII) and Tc(IV). Under atmospheric or moderately oxidizing environment, Tc is manifested as pertechnetate ($^{99}\text{TcO}_4^-$); while under a moderately reducing environment, $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and TcS_2 become the predominant species (Lukens et al., 2002; Kaplan, 2003; Ashworth and Shaw, 2005). Pertechnetate is highly soluble, and it does not significantly sorb onto mineral surfaces, soils, or sediments, and thus, migrates at nearly the same velocity as groundwater under common subsurface conditions (Bruggeman et al., 2007). Consequently, TcO_4^- can be readily taken up by plants and enter the food chain through the similar mechanisms as sulfate and phosphate (Watson and Ellwood, 2003; Jaisi et al., 2009). In contrast, the Tc(IV) species are sparingly soluble and display a strong reactivity with mineral surfaces (Livens et al., 2004; Um et al., 2011). For example, the solid-water distribution coefficient (K_d) for TcO_4^- is $<10 \text{ L kg}^{-1}$, but is on the order of 10^3 L kg^{-1} for Tc(IV) (Lieser and Bauscher, 1987; Kershaw, 1992; Kershaw et al., 1992). Therefore, the reduction of Tc(VII) to Tc(IV) can potentially sequester mobile Tc in contaminated soils and groundwater (Jaisi et al., 2009; Burton-Pye et al., 2011).

Various adsorbents or reductants have been tested to immobilize/remove Tc(VII) from contaminated water, including ion exchange resins (Bond et al., 1999; Cao et al., 2011), activated carbon (Holm et al., 2000; Wang et al., 2007), aluminum (hydr)oxides (Stewart et al., 2004; Peretyazhko et al., 2008b), anatase (Stewart et al., 2004), zero-valent iron (Darab et al., 2007; Ding et al., 2013; Liu et al., 2013), various reducing bacteria (Jaisi, 2007; Li and Krumholz, 2008; Dolor et al., 2009; Plymale et al., 2011), and iron oxides (Liu and Fan, 2005; Plymale et al., 2011). For instance, Liu and Fan (2005) studied adsorption of Tc(VII) on iron-bearing materials, and observed that the adsorption ratios were about 3500, 1200, and 300 mL/g for Fe, Fe_3O_4 , Fe_2O_3 , respectively under anoxic conditions, and the adsorption ratios decreased with increasing pH in the range of 5–12. Vinsová et al. (2006) studied adsorption characteristics of ^{99}Tc onto bentonite with different additives (Fe, FeS, Fe_3O_4 and activated carbon) under anaerobic conditions, and they observed that Fe and FeS were able to facilitate reduction of pertechnetate to insoluble $\text{TcO}(\text{OH})_2$ or $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, while the main mechanism of retention on activated carbon was physical sorption.

Studies on interactions of Tc with iron (oxy)hydroxide and sulfide minerals have shown that the reduced Tc(IV) species can be strongly associated with iron (Wharton et al., 2000; Jaisi, 2007; Um et al., 2011; Yang et al., 2012). In anoxic environments, both Fe(II) and S(-II) are effective Tc(VII) reductants (Peretyazhko et al., 2012). Peretyazhko et al. (2008b) investigated heterogeneous reduction of Tc(VII) by Fe(II) adsorbed on Al (hydr)oxides (R-AlOOH) and corundum (R- Al_2O_3), and observed that Tc(VII) was completely reduced within 11 days, and the final heterogeneous redox product on corundum was Tc(IV) oxyhydroxide, $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, based on EXAFS analysis. Other investigations also showed that Fe(II) minerals can reduce TcO_4^- and lead to sorption on mineral surfaces (Bondietti and Francis, 1979; Zachara et al., 2007; Geraedts and Maes, 2008). Um et al. (2011) observed that synthetic goethite (α - FeOOH) combined with aqueous Fe(II) was able to sequester Tc, where Fe(II) acts as an efficient electron donor on the surface of

goethite, and the results suggested that Tc was reduced and incorporated within the goethite lattice, which was hardly releasable, even when the final Tc-goethite product was exposed to oxidizing conditions. Liu et al. (2008) reported that amorphous FeS was able to reduce TcO_4^- to TcO_2 , and the reaction was accelerated with increasing ionic strength and was strongly pH-dependent. Livens et al. (2004) studied reaction between TcO_4^- and mackinawite, and found a TcS_2 -like species in the products. Wharton et al. (2000) carried out an X-ray Absorption Spectroscopy study of co-precipitated Tc with mackinawite (FeS), and found that TcO_4^- was reduced to Tc(IV) upon coprecipitation with FeS and a TcS_2 -like phase was formed. When the host lattice was oxidized, the reduced Tc remained as a TcO_2 phase. Liu et al. (2007) showed that the reaction between TcO_4^- and sulfide under anaerobic conditions results in Tc_2S_7 in an alkaline aqueous solution.

Pyrite (FeS_2) is one of the most common rock-forming minerals on the Earth's surface and is thermodynamically more stable than other Fe sulfides under a range of environmental conditions. In recent years, a number of studies have revealed that pyrite could remove various organic and inorganic pollutants from water (Lee and Batchelor, 2002; Borah and Senapati, 2006; Oh et al., 2008). Others found that pyrite can reduce and remove U(VI) and Se(VI) (Aubriet et al., 2006; Breynaert et al., 2008; Kang et al., 2011). Hu et al. (2008) pointed out that the presence of Fe(II) in FeS_2 in the host rock could reduce Tc(VII) to Tc(IV). Bruggeman et al. (2007) and Maes et al. (2004) studied the reaction between TcO_4^- and natural pyrite through EXAFS measurements, and found that the end product is a $\text{TcO}(\text{OH})_2$ polymer or colloid ($\log K^{\text{TcO}(\text{OH})_2} = 5.30 \pm 0.30$). However, information has been lacking on the effectiveness of using synthetic pyrite particles for remediation of contaminated soil and groundwater.

The overall goal of this research was to investigate the feasibility of using synthetic pyrite particles for reductive immobilization of TcO_4^- in soil and groundwater. The specific objectives were to: 1) prepare reactive pyrite particles; 2) examine the reaction kinetics of the pyrite particles for reduction and removal of Tc(VII) from water through batch experiments; 3) elucidate the underlying mechanisms governing Tc immobilization; 4) determine effects of particle dosage, pH, and DOM on the reduction/removal efficacy; and 5) test the effectiveness of the material for in situ immobilization of Tc(VII) in a model soil in a setting simulating the permeable reactive barrier (PRB).

2. Materials and methods

2.1. Materials

The following chemicals (analytical-grade or higher) were used as received: ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and sodium hydrosulfide ($\text{NaHS} \cdot x\text{H}_2\text{O}$) (71.7%) from Sigma-Aldrich (St. Louis, MO, USA), hydrochloric acid, sodium hydroxide, sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2 \cdot 3\text{H}_2\text{O}$), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) (Fisher), and 2-(N-morpholino) ethanesulfonic acid (MES, $\text{C}_6\text{H}_{13}\text{NO}_4\text{S}$) from Fisher (Fisher Scientific, Pittsburgh, PA, USA), Ultima Gold liquid scintillation cocktail (Packard Instrument Company, USA), ammonium pertechnetate ($\text{NH}_4^{99}\text{TcO}_4$) (FOB Eckert & Ziegler Isotope Products, Valencia, CA, USA). All solutions were prepared with 18-M Ω deionized (DI) water.

A sandy soil was taken from the Auburn University E.V. Smith Research Center (Tallassee, AL, USA). Before use, the soil was washed with tap water 5 times to remove fine colloids and water soluble components (An and Zhao, 2012). The soil was air-dried at room temperature and sieved through a screen of 2 mm openings. Soil analyses were performed by the Soil Testing Laboratory at Auburn University. The key soil properties include: OM (organic

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