Photoreduction of Tc-99 Pertechnetate to Low-valent Tc(IV) Using Titanium Dioxide

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ABSTRACT

Technetium-99 (^{99}Tc) is a fission product present in large amounts in nuclear waste sites. It has nine oxidation states and long half-life (211,000 yr). Pertechnetate, TcO_4^- as the most stable form in aerobic environment makes ^{99}Tc challenging to isolate and stabilize during nuclear waste disposal. The immobilization of ^{99}Tc has been achieved via reduction of $Tc(VII)O_4^-$ to relatively insoluble $Tc(IV)O_2$, which is then immobilized in glass or ceramic. Here, we investigate TiO_2 as a photocatalyst to reduce Tc^{+7} to Tc^{+4} upon UV irradiation. X-ray Absorption Spectroscopy shows reduction to Tc^{+4} in the solution and on the surface of TiO_2 nanoparticles up to 90%. We postulate that TiO_2 can be a waste form for the incorporation of Tc^{+4}.

INTRODUCTION

A waste form to immobilize Tc must be durable and prevent release of Tc until an acceptable fraction has decayed. The most commonly used waste form, borosilicate glass, is durable, but loss of volatile Tc species during glass vitrification makes it difficult to retain Tc in the glass. Titanium dioxide, TiO_2 is desirable material since it's cheap, durable and non-toxic. It is a photoactive semiconductor with a wide band gap (3.2eV) and has been studied as a photocatalyst for water splitting, as a photooxidizer of organic pollutants and as a reductant of metal ions. Upon illumination with UV light, electrons are promoted from the valence band (VB) to the conduction band (CB) to form a charge separated state, i.e., an electron (e^-)-hole (h^+) pair . The (h^+) in the VB and (e^-)in the CB migrate to the surface. These (e^-) and (h^+) in the CB and VB can oxidize or reduce different species in solutions. We hypothesize that pertechnatate $Tc^{7+}O_4^-$ can be reduced to a lower valent state either in solution, on the surface of TiO_2, or even within the TiO_2 lattice. The band positions of TiO_2 are sufficient for redox transformation of environmental pollutants, including TcO_4^- .

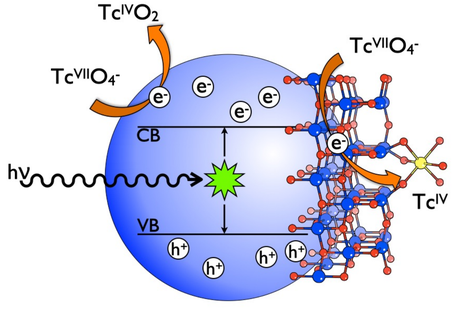

Fig 1. Proposed strategy for photoreduction of TcO_4^- by TiO_2 in solution and on the surface

EXPERIMENTAL

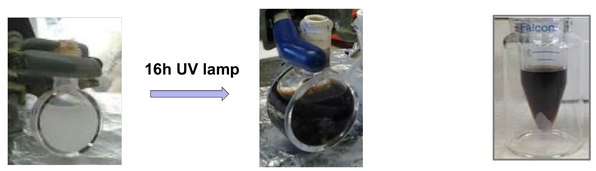

Fig 2. Left: Suspension of 5 mM TcO_4^- with 10 mg of TiO_2 in reduction solution pH 1.18 (H_2SO_4, D_2O, and IPA, 2:1:1 by vol.). Suspension turns dark brown color characteristic for the reduced Tc species after 16 hr of irradiation with UV lamp. Right: Centrifuged brown colored particles.

RESULTS AND DISCUSSION

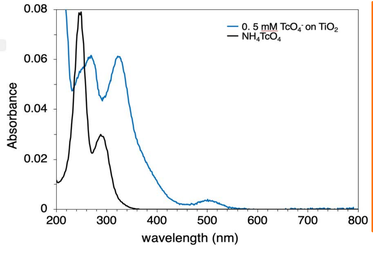

Fig 3.UV-Visible spectra after 16 h of irradiation with UV lamp: (black) control TcO_4^-, (blue) supernatant bands at 280 nm, 330 nm and 510 nm indication of reduced Tc^{4+} species.

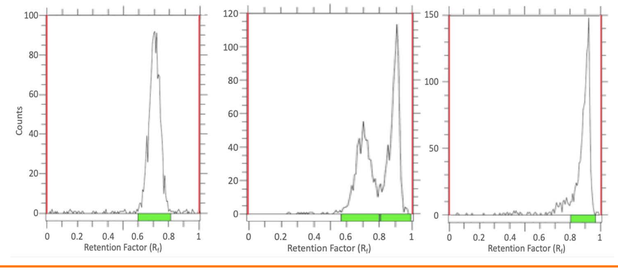

Fig 4. ITLC data of supernatant after UV irradiation. (Left) TcO_4^- control , (middle) supernatant from the irradiated TcO_4^- in solution with TiO_2 ,(right) fully reduced Tc^{4+} in solution.

XANES and EXAFS analysis show Tc^{4+} in the supernatant and adhered to the TiO_2. Tc^{4+} species are a polymeric form of Tc (IV) oxide -Tc-(μ-O)$_2$-Tc structure or $TcO_2 \cdot 2H_2O$ surface precipitate.

Table 1. XANES data for selected samples at pH 1.13. All samples are 10 mM TcO_4^-, 10 mg TiO_2, and 16 h irradiation with UV source (254 nm).

	Supernatant		Solid TiO_2 NP	
Percent,%	**Tc^{4+}**	**Tc^{7+}**	**Tc^{4+}**	**Tc^{7+}**
TiO_2 and TcO_4^- (with IPA)	89 (1)	11(2)	88(1)	12(2)
Controls:				
TiO_2 and TcO_4^- (without IPA)	10(1)	90(1)	80(1)	20(2)
TcO_4^-, no TiO_2 (with IPA)	24(1)	76(1)		
TcO_4^-, no TiO_2 (without IPA)	2(1)	98(1)		

CONCLUSIONS

We have identified a strategy to reduce pertechnetate, TcO_4^- cleanly and efficiently using the semiconductor TiO_2 as a photocatalyst that forms stable Tc^{+4} species in direct contact with TiO_2 nanoparticles and in solution.

XANES analysis shows that photoreduction with TiO_2 resulted in ~ 90% Tc^{+4} in solution. Tc adsorbed to the TiO_2 was largely in the form of Tc^{+4}. This study can provide a fundamental understanding of the chemistry of Tc, as well as photocatalytic reduction of TcO_4^- by TiO_2 nanomaterials at concentrations relevant to reprocessing.

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