

Investigating the complex interaction of Technetium with magnetite nanoparticles

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Nanoparticles (NPs) are relevant in medicine, catalysis and environmental remediation. Among them, magnetite (Fe(II)Fe(III)₂O₄) NPs are especially interesting due to their redox and magnetic properties and their tunability of size and surface properties, which makes them suited for the removal of many redox-active pollutants. Tc is of great concern for the safety assessment of nuclear waste repositories, since ⁹⁹Tc is a fission product with a long half-life ($t_{1/2} = 2.1 \times 10^5$ years). Under oxidative conditions Tc forms an anionic species, pertechnetate (Tc(VII)O₄⁻), which is mobile due to its weak interactions with minerals. Under anaerobic conditions, pertechnetate is reduced by reducing agents to Tc(IV), which sorbs on minerals, forms insoluble oxides like TcO₂, or is structurally incorporated by stable natural minerals. [1]

Previous studies by Yalcintas *et al.* [2] suggested that Tc(VII) reduction by magnetite resulted in the precipitation and surface adsorption of TcO₂-like oligomers at pH 9, i.e. close to the pH of magnetite solubility minimum, while reduction at lower pH of 6-7 resulted in a partial incorporation of Tc(VI) in octahedral Fe sites of magnetite [3]. A working hypothesis was that the incorporation happens only at higher magnetite solubility, while the final retention mechanism remains enigmatic. Thus, our investigations are aimed to carry out a systematic approach covering a wide pH range (3-13), initial Tc concentration ([Tc] = μM-mM) and equilibration time ($t_{eq} = 1-210$ days).

The results show that magnetite removes at least 98 % dissolved Tc. To characterize the molecular geometry of the Tc vicinity, mainly X-ray absorption spectroscopy (XAS) has been used. XANES analysis reveals the predominance of Tc(IV) at all evaluated pH values, supporting that reductive Tc immobilization is the main retention mechanism. A detailed EXAFS analysis with different preparation methods (sorption, coprecipitation, Fe(II)-recrystallization) is currently underway to elucidate the molecular structure of the retained Tc species.

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[1] A.H. Meena, Y. Arai, *ENVIRONMENTAL CHEMISTRY LETTERS*, 2017, **15**, 241.