

Zn(II) sorption on nanoparticulate UO₂

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Nanoparticulate UO₂ is considered to play a significant role in the transport of uranium in the environment and the precipitation of nanoparticulate UO₂ can be biologically mediated. It is therefore critical to evaluate the differences in chemical properties of the nanoparticulate material, with respect to what is known regarding bulk material. In an attempt to understand the differences in surface reactivity of nanoparticulate UO₂ and bulk uraninite, we have examined the sorption of aqueous Zn(II) on both forms of UO₂ using batch uptake experiments and Zn K-edge EXAFS spectroscopy. Precipitation of biogenic UO₂ was mediated by *Shewanella putrefaciens* CN32 and was treated with two washing protocols: (1) a NaOH-KHCO₃ wash to remove surface organic matter and soluble uranium, or (2) a KHCO₃ wash to remove soluble uranium. BET determined surface area of the two washed samples of biogenic UO₂ and abiotic UO₂ are 128 m²g⁻¹, 95.6 m²g⁻¹, and 0.0633 m²g⁻¹, respectively; particle size of the biogenic UO₂ is 2-10 nm as determined by FEG-SEM. Aqueous Zn(II) adsorption was studied as a function of sorption density (0.009 to 2.6 μmoles*m⁻²) and a background electrolyte concentration (1 to 100 mM NaCl) at pH 7. The batch uptake experiment indicated that aqueous Zn(II) adsorption is independent of the electrolyte concentration, suggesting an inner-sphere binding mechanism on all three UO₂ substrates. Fits of the Zn K-edge EXAFS indicate that Zn sorption is dependent on the washing treatment of biogenic UO₂. One Zn-U neighbor at 2.75 Å was observed for the NaOH wash, but not the KHCO₃ wash, suggesting that Zn(II) sorbs directly to the UO₂ surface in the first case, and possibly to organic matter in the latter. A FEFF-generated Zn K-edge EXAFS spectrum of Zn(II) adsorbed on the UO₂ surface in a bidentate mode agrees well with the experimental data. The results presented here indicate that the presence of organic matter associated with the biogenic UO₂ surface changes its surface reactivity, and its absence or presence needs to be taken into account when studying the fate and transport of uranium in the environment.