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Title: PLUTONIUM(VI) SORPTION TO MANGANESE DIOXIDE

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Plutonium(VI) Sorption to Manganese Dioxide

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Introduction

Redox-active metal oxides may strongly affect the environmental behavior and mobility of actinides. Manganese oxides are relatively common redox-active soil components, which have a high surface area and which some studies show sorb plutonium selectively over other mineral phases.[1] For plutonium, oxidation states that could exist in the environment include +III to +VI, with Pu(IV) being predominant in the insoluble phase. Plutonium(V), and to a lesser extent Pu(VI), are the stable Pu oxidation states in solution under environmental conditions.[2] We are using synthetic δ-MnO_2 because it is most similar to the common natural manganese oxide mineral birnessite. Previously, we have shown that Pu(V) is oxidized to Pu(VI) in solution by δ-MnO_2, then very effectively sorbed to the mineral. We are now studying Pu(VI) sorption to synthetic δ-MnO_2 in detail to determine its sorption mechanisms and sorption capacity.

Results

A series of sorption experiments were conducted at pH 3 to avoid Pu(VI) hydrolysis and still be at conditions near or above the point of zero charge of δ-MnO_2 so that it has a net negative surface charge. Titration experiments were performed where aliquots of Pu(VI) were added to aqueous solutions containing 1 mg δ-MnO_2 / mL. The solutions were allowed to equilibrate a set time after each Pu aliquot addition and then the concentration of Pu(VI) remaining in the separated solution phase was determined by liquid scintillation counting and visible/near-IR spectroscopy. Batch sorption experiments were also performed of 3×10^{-5} M to 3×10^{-3} M Pu(VI) with mineral suspensions of 1 mg δ-MnO_2 / mL. Figure 1 shows the Pu(VI) sorption capacity of δ-MnO_2 as a function of Pu(VI) solution concentration. Experiments suggest the sorption capacity of manganese dioxide at pH 3 is approximately 0.1 mmol Pu(VI) / g δ-MnO_2, with small changes in pH influencing the capacity. The rate of Pu(VI) sorption at pH 3 was also studied and found to be rapid, with approximately 80% of the equilibrium Pu(VI) concentration sorbed onto MnO_2 within the first hour of contact.

The pH dependence of Pu(VI) sorption onto δ-MnO_2 is being studied at variable Pu(VI) concentrations. At 1×10^{-5} M Pu(VI) and pH 5-7, Pu(VI) is essentially completely sorbed to MnO_2, while some Pu remains in

solution at lower and higher pH (Figure 2a). The low percentage Pu(VI) bound below pH 4 is interpreted as a result of decreasing negative charge on MnO_2, which results in less sorption of PuO_2^{2+}. Pu(VI) binding decreases as the pH is raised above 6.5, where Pu(VI) increasingly exists as neutral and negatively-charged hydroxo and carbonato species.
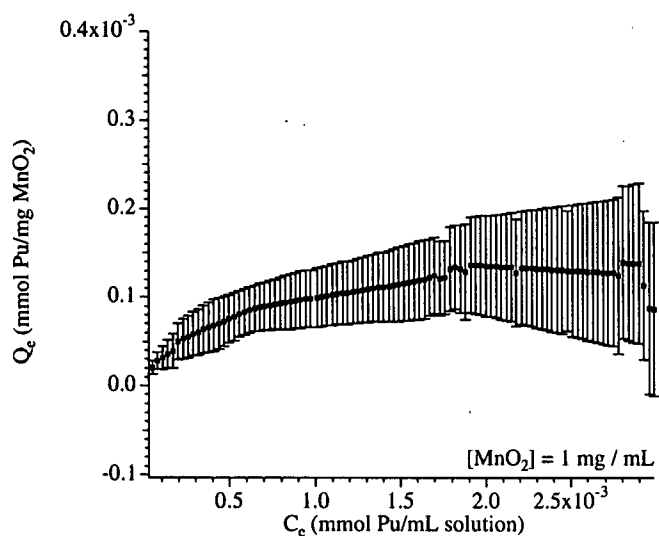

Figure 1. Pu(VI) sorption capacity of δ-MnO_2 in 0.1 M ionic strength aqueous solution at pH 3. C_e and Q_e are the equilibrium Pu(VI) concentrations in solution and on the MnO_2 adsorbent, respectively.
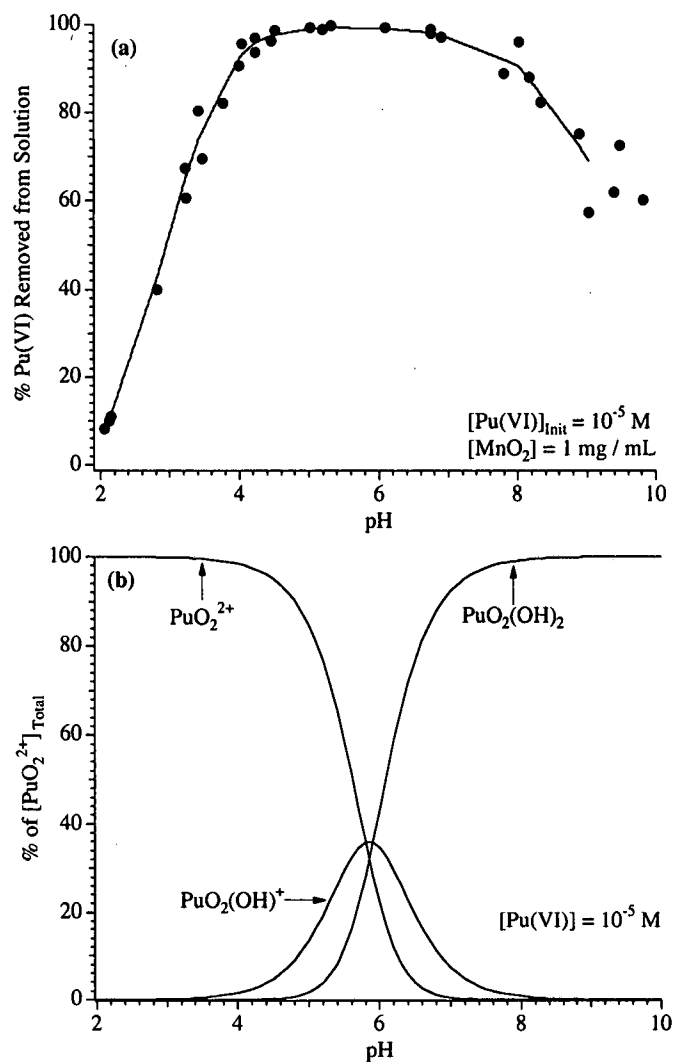

Figure 2. (a) pH-dependent sorption of Pu(VI) on δ-MnO_2 in 0.1 M ionic strength aqueous solution. Circles represent data from several independent experiments and the line is their average. (b) Pu(VI) hydrolysis species distribution plot as a function of pH.

In order to interpret the sorption data we also need to know the solution speciation of Pu(VI) in the absence of the mineral. We are investigating and characterizing Pu(VI) hydrolysis species using potentiometric and spectrophotometric methods. Our studies on 10^{-2} M to 10^{-3} M Pu(VI) solutions indicate the formation of dimeric hydrolysis species $[PuO_2OH]^{2+}$ and $[PuO_2(OH)_2]_2$. At lower Pu(VI) concentrations, 10^{-4} M, data suggest a change in speciation and the presence of monomeric hydrolysis species. The species diagram Figure 2b, calculated for Pu(VI) at the same concentration as that in sorption experiments shown in Figure 2a, shows that the decrease in Pu(VI) sorption coincides with onset of formation of Pu(VI) hydroxo species.

Discussion

Manganese dioxide has a high surface area and oxidizes Pu(V) to Pu(VI) and rapidly sorbs it. The observed sorption behavior of Pu(VI) onto δ-MnO_2 correlates well with Pu(VI) solution speciation. Plutonium(VI) sorption onto δ-MnO_2 begins at a lower pH than, for comparison, U(VI) sorption onto Fe_2O_3, consistent with the lower point of zero charge of δ-MnO_2.[3] Modeling of this sorption data using site sorption models is in progress. Additional Pu(VI) sorption data will be presented and compared to data collected for U(VI). Comparisons to actinide sorption onto other mineral phases will also be presented.

References

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