The Effect of pH on the Sorption and Speciation of U(VI) in $Ca^{2+}/UO_2^{2+}/CO_3^{2-}$ - SiO_2 System

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1. Introduction

Uranium is the most common radioactive contaminant in the subsurface environment [1,2]. It has been found that the calcium-uranyl-carbonate complexes $Ca_2(UO_2)(CO_3)_3(aq)$ and $Ca(UO_2)(CO_3)_3^{2-}$ dominate U(VI) speciation in neutral to weakly alkaline conditions and are the major aqueous U(VI) species in natural settings [3,4]. Therefore, studying the interactions of $Ca^{2+}/UO_2^{2+}/CO_3^{2-}$ complexes with minerals is necessary to understand and accurately predict the uranium behavior, i.e. fate and transport, in the environment. The present research seeks to investigate the sorption behavior of $Ca^{2+}/UO_2^{2+}/CO_3^{2-}$ complexes on silica. Batch sorption experiments and spectroscopic analysis are combined to infer mechanisms of U(VI) sorption on silica surface.

2. Methods

The silica used in the present study was purchased from Aldrich and it has the specific surface area of 558.48 ± 2.05 m^2/g and the mean particle size of 15.5 ± 2.2 nm. According to the solid:liquid (S:L) ratio, an appropriate amount of silica was weighed into 50 mL polypropylene vial. Then 20 mL of $Ca^{2+}/UO_2^{2+}/CO_3^{2-}$ aqueous solution were added, and the pH was adjusted. The sorption vials were shaken for 7 days at 100 rpm and 25 °C. After equilibration, the samples were centrifuged at 4400 rpm for 30 minutes and the supernatants were filtered with 0.45 µm membrane filter. The aqueous concentration of uranium was measured in the filtrate using ICP-MS. The amount of adsorbed U(VI) was calculated as the difference between the total U(VI) concentration and the aqueous U(VI) concentration at equilibrium. Desorption experiments were conducted using ethylenediaminetetraacetic acid (EDTA) in background electrolyte solution of the same pH and ionic strength. After sorption equilibration and phase separation, the supernatant and U-loaded silica were analyzed using time-resolved laser fluorescence spectroscopy (TRLFS) to analyze aqueous and adsorbed U(VI) species, respectively.

3. Results and Discussion

In this section, data obtained from batch sorption-desorption experiments and spectroscopic measurements are presented and discussed from a mechanistic point of view.

3.1 The pH dependency

The influence of the solution pH (i.e. sorption edge) on U(VI) sorption on silica is presented in Fig. 1. The U(VI) sorption was quantitative at low pH values and decreased with increasing pH because of the formation of $Ca(UO_2)(CO_3)_3^{2-}$ and $UO_2(CO_3)_3^{-4}$ complexes. These negatively charged complexes cause electrostatic repulsion with silica surface which is also negatively charged in this pH range. Stewart et al. [4] have reported an inverse relationship that an increase in either pH or Ca^{2+} concentration decreases the amount of U(VI) adsorption at goethite surface due to the formation of uranyl-calcium-carbonato complexes. In the present system, the sorption affinity of nano-size silica mitigated the adverse effect of pH such that the U(VI) sorption was more than 75% even at high pH values.
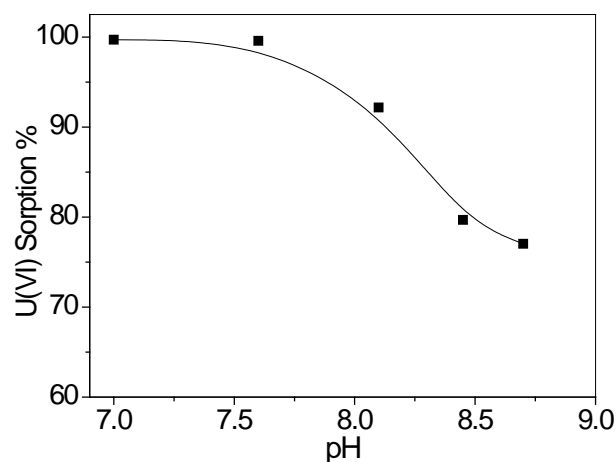

Fig. 1. Effect of pH on U(VI) sorption; [U(VI)]$_{initial}$ = 10^{-4} M, [Ca^{2+}] = 10^{-3} M, [CO_3^{2-}] = 5×10^{-3} M, I = 0.1 M NaClO$_4$, S:L = 0.5 g/L.

3.2 Desorption of U(VI)

Uranium was sorbed on silica at different pH values, then it was desorbed using 0.01 M EDTA solution. The U(VI) desorption is plotted versus reaction time in Fig. 2. The U(VI) desorption occurred relatively fast at pH 8.8 and reached 44% within 3 days and then increased slowly. At lower pH values 7.3 and 8.1, it took much longer time (~30 days) to reach equilibrium. After 60 days, the U(VI) desorption reached ~51% at pH 8.8, and ~40% at pH 7.3 and 8.1. The slower and lower U(VI) desorption at lower pH values indicates that the U(VI)

complex sorbed favorably at lower pH values is more strongly bound to the silica surface than the U(VI) complex favorably sorbed at higher pH values.
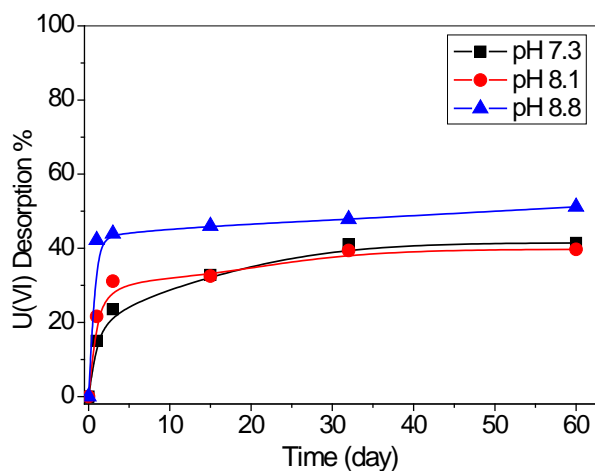

Fig. 2. Desorption of U(VI) with EDTA; $[Ca^{2+}] = 10^{-3}$ M, $[CO_3^{2-}] = 5 \times 10^{-3}$ M, [EDTA] = 10^{-2} M, I = 0.1 M NaClO$_4$, S:L = 0.5 g/L.

3.3 TRLFS studies

After sorption equilibrium and phase separation, the aqueous and solid phases were analyzed using TRLFS. The fluorescence spectra of aqueous and sorbed U(VI) species were normalized and presented in Fig. 3. The spectrum of aqueous U(VI) species has fluorescence peaks at 466, 485, 505, 527, 550 and 576 nm which agree with those reported in literature for $Ca_2(UO_2)(CO_3)_3$(aq) and $Ca(UO_2)(CO_3)_3^{2-}$ aqueous complexes [3,5]. The spectrum of U(VI) sorbed species has fluorescence peaks at 506, 528, 551 and 576 nm. However, the fluorescence peaks at 466 nm and 485 nm could not be observed in the spectrum of U(VI) sorbed species. This change in the U(V) fluorescence spectral shape was presumably due to the change in the U(VI) chemical environment upon sorption.
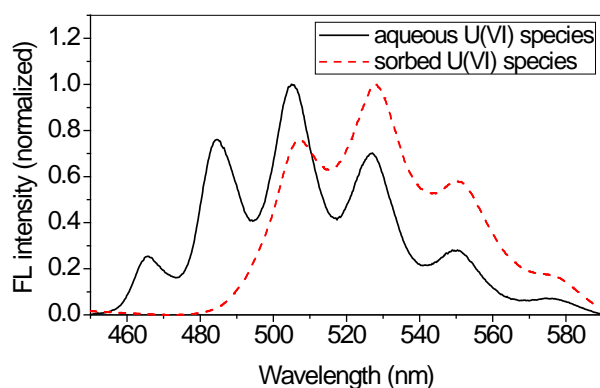

Fig. 3. Fluorescence spectra of $Ca^{2+}/UO_2^{2+}/CO_3^{2-}$ aqueous complexes and U(VI) sorbed species; [U(VI)]$_{initial}$ = 10^{-4} M, $[Ca^{2+}]=10^{-3}$ M, $[CO_3^{2-}] = 5 \times 10^{-3}$ M, I = 0.1 M NaClO$_4$.

The TRLFS analysis of adsorbed U(VI) was performed at different pH values. The fluorescence peak locations and lifetimes of U(VI) sorbed species are presented in Table I. The U(VI) complexes sorbed at different pH values have similar fluorescence peak positions and the decay of the fluorescence intensity always indicates the presence of two U(VI) surface complexes A and B with two fluorescence lifetimes τ_1 and τ_2, respectively.

Table I. Fluorescence spectral characteristics of U(VI) species sorbed on silica

pH	Peak maxima (nm)	Life time (µs)	
		τ_1	τ_2
7.2	506, 527, 550, 574	261	840
7.8	506, 527, 550, 575	248	794
8.7	506, 527, 550, 575	243	787

Figure 4 shows the TRLFS analysis of U(VI) surface complexes formed at different pH values and contact times. The delay time and gate width were varied to monitor the changes in the spectra of U(VI) surface complexes. With increasing the pH, the spectrum of the short-lived surface complex approaches marginally, yet steadily, the spectrum of the long-lived surface complex. In fact, the normalized relative ratio of the fluorescence intensities of the two U(VI) surface complexes (A:B) decreases with increasing pH, which indicates a steady decrease in the ratio of the two U(VI) surface complexes. Combining wet chemistry and spectroscopic analysis, it could be concluded that the U(VI) complex "A" with shorter lifetime is more strongly bound to silica surface than the U(VI) complex "B" with longer lifetime, and the decrease of U(VI) sorption affinity with the increase of pH is due to the decrease in the ratio of the two U(VI) surface complexes.

4. Conclusion

In environmental conditions of circumneutral to alkaline pH and in presence of calcium and carbonate ions, calcium-uranyl-carbonate complexes dominate aqueous U(VI) speciation. Under these conditions, U(VI) can be sorbed on silica and thereby its transport is retarded. However, the speciation of adsorbed U(VI) and hence its sorption affinity depend on the solution pH. Therefore, the pH has to be considered in disposal and remediation programs involving uranium-contaminated waste and land.
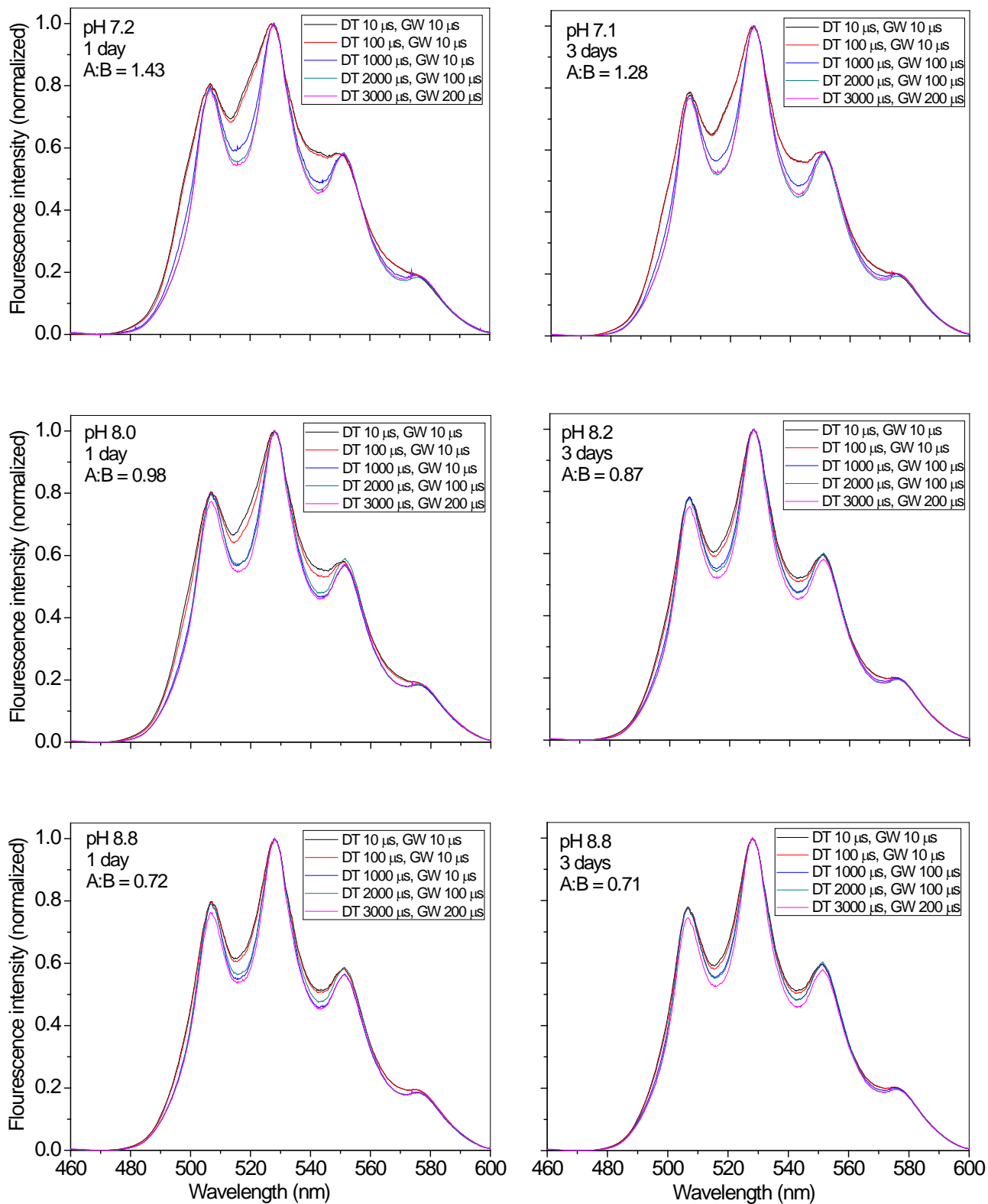
Fig. 4. Fluorescence spectra of U(VI) complexes sorbed at different pH values; $[U(VI)]_{aq,initial} = 10^{-5}$ M, $[Ca^{2+}] = 10^{-4}$ M, $[CO_3^{2-}] = 10^{-3}$ M, I = 0.1 M NaClO$_4$, S:L = 5 g/L. pH, contact time and A:B relative ratio are shown in the upper left corners.

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