

The Influence of Humic Acid and Colloidal Silica on the Sorption of U(VI) onto SRS Sediments Collected from the F/H Area - 15499

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ABSTRACT

Between 1955 and 1988, the F/H Area Seepage Basins located in the center of SRS received approximately 6,814,000 m³ of acidic waste solutions containing radionuclides and dissolved metals. Uranium (VI) is a key contaminant of concern in groundwater associated with the basins. The pump-and-treat water treatment unit designed and built in 1997 to remove metals and radionuclides eventually became less effective, prompting research for new remedial alternatives. The pump-and-treat system was discontinued in 2004, replaced with a funnel-and-gate system in which base solutions are injected at the gates to raise pH. To take advantage of the potential formation of uranium silicate minerals, Florida International University - Applied Research Center (FIU-ARC), in collaboration with Savannah River National Laboratory (SRNL), is conducting an investigation into a base containing sodium silicate to evaluate whether these solutions have sufficient alkalinity to correct the acidic nature of the aquifer sediments. The research was extended to investigate if U(VI) is bound to colloidal silica and if any synergy exists between humic acid (HA) and colloidal Si that would influence the removal of uranium. Humic substances (HS) are a major component of soil organic matter and are known for their abilities to influence the migration behavior and fate of heavy metals. Studies showed that HA function as an important ion exchange and metal-complexing ligand, carrying a large number of functional groups with high complexing capacity that can greatly affect the mobility behavior of actinides in natural systems. The study investigates if there are any synergistic interactions between U(VI) ions, humic acid and colloidal silica under oxidized conditions and studies the influence of HA and Si on the sorption of U(VI) onto sediments collected from the F/H Area. The experiments also evaluated the effects of different environmental variables such as pH, presence of U(VI) and varying concentrations of HA on the sorption behavior of U(VI) in multi-component batch systems in the pH range between 3 and 8. Several background sediment samples were collected at SRS from archived cores obtained during installation of the well FSB 91C and used for preparation of triplicate samples. The experimental matrix was set up as follows:

- Batch 1: Si (3.5 mM) + U (VI) (0.5ppm) (no sediments and no HA)
- Batch 2: Si (3.5 mM) + U (VI) (0.5ppm) + HA (10 ppm) (no sediments)
- Batch 3: U (VI) (0.5 ppm) + HA (10ppm) (no Si and no sediments)
- Batch 4: Sediments + Si (3.5 mM) + U (VI) (0.5 ppm) (no HA)
- Batch 5: Sediments + Si (3.5 mM) + U (VI) (0.5 ppm) + HA
- Batch 6: Sediments + U (VI) (0.5 ppm) + HA, (no Si)
- Batch 7: Sediments + U (VI) (0.5 ppm) (no Si and no HA)

All samples were prepared in triplicate 50-mL conical tubes. All control and experimental tubes were vortexed and kept on a shaker for 24 h at 100 rpm and room temperature.

Results showed that the sediment-bearing batches typically exceeded the performance of non-sediment batches. Results showed that the sorption of U(VI) onto sediments was influenced by the pH and the presence of HA. At low pH 3, the addition of HA slightly enhances U(VI) sorption compared to the HA-free samples. This result is consistent with other studies; in the acidic pH range, the addition of HA slightly enhances U(VI) sorption relative to the HA-free system. Conversely, in the pH range of 4 to 7, the sorption of U(VI) on Si was reduced in the presence of HA in comparison to the system without HA. In subsequent experiments the concentration of HA will be increased to 50ppm.

INTRODUCTION

Savannah River Site (SRS), located 13 miles south of Aiken in South Carolina, was a defense nuclear processing facility owned by the U.S. government. During the Cold War, from 1953 to 1988, SRS produced a large amount of radioactive and hazardous acidic waste from the production of plutonium and irradiated fuel. The acidic waste solutions containing low-level radioactivity from numerous isotopes were discharged to a series of unlined seepage basins in the F/H Area. At that time, it was believed that most of the radionuclides present in the waste solution would bind to the soil, precluding the migration of the radionuclides. However, sufficient quantities of uranium isotopes, ^{129}I , ^{99}Tc , and tritium migrated into the groundwater to create an acidic plume with a pH between 3 and 5.5. In an effort to remove the contaminants from the groundwater, pump-and-treat and re-inject systems were implemented in 1997. Down gradient contaminated groundwater was pumped up to a water treatment facility, treated to remove metals (through osmosis, precipitation/flocculation, and ion exchange), and then re-injected upgrade within the aquifer. The pump-and-treat water treatment unit eventually became less effective, generated large amounts of radioactive waste and was expensive to maintain, prompting research for new remedial alternatives. In 2004, the pump-and treat system was replaced by a funnel and gate system in order to create a treatment zone via injection of a solution mixture composed of two components, sodium hydroxide and carbonate. The injections were done directly into the gates of the F-Area groundwater to raise pH levels. The purpose of the treatment zone was to reverse the acidic nature of the contaminated sediments, thereby producing a more negative net charge on the surface of sediment particles and thus enhancing adsorption of cationic contaminants. This system of remediation required a systematic re-injection of the base to raise the pH to near neutral values. However, the continuous use of high concentrations of a carbonate solution to raise pH creates a concern of possible re-mobilization of uranium that was previously adsorbed within the treatment zone since U(VI) in the presence of bicarbonate ions forms soluble aqueous uranyl-carbonate complexes.

Bethke (2006) suggested a disodium silicate base solution to treat acidic groundwater. For contaminant plumes containing uranium, this would not only enhance sorption but has the potential to sequester uranium in low solubility uranium silicate minerals. Savannah River National Laboratory (SRNL) began studying the feasibility of a sodium silicate base as part of an applied research initiative at the F/H Areas funded by the U.S. Department of Energy and is now collaborating with the Florida International University - Applied Research Center (FIU-ARC) to continue these studies. In addition, the research has been extended to investigate if any synergy exists between humic acid (HA) and silicates that would influence the removal of uranium from the solutions.

Humic substances are ubiquitous in the environment, occurring in all soils, waters, and sediments of the ecosphere. Humic substances consist of complex organic compounds formed by the decomposition of plant and animal tissue. This decomposition process is known as humification, where the organic matter is transformed naturally into humic substances by microorganisms in the soil. Humic substances are divided into three main fractions: humic acid (HA), fulvic acid (FA), and humin. Their size, molecular weight, elemental composition, structure, and the number and position of functional groups vary. Studies showed that HA is as an important ion exchange and metal-complexing ligand, carrying a large number of functional groups with high complexing capacity that can greatly affect the mobility behavior of actinides in natural systems [2, 3, 4]. pH and concentration are the main factors affecting the formation of complexes between humic molecules and metals. It is generally considered that the sorption of metal ions on the mineral surfaces in the presence of HA is enhanced at low pH and reduced at high pH [5].

The focus of these experiments was to investigate if there are any synergistic interactions between U(VI) ions, humic acid and silica under oxidized conditions and study the influence of HA and Si on the sorption of U(VI) onto sediments collected from the F/H Area.

EXPERIMENTAL PROCEDURE

A multi-component batch system was used to study the removal behavior of uranium from pH 3 to 8. Six sediment samples collected at depths 19.81 m (65 ft), 24.38 m (80 ft), 27.43 m (90 ft), 28.96 m (95 ft), 30.48 m (100 ft), and 32.0 m (105 ft) at Savannah River Site from the well FSB 91C were used in this experiment. First, a 10-g soil sample from each depth was weighed and mixed to create a 60-g soil mixture. After mixing the soil thoroughly, it was used for the preparation of soil-bearing batches at the soil to water ratio of 1:20. The experimental matrix was set up as follows:

- Batch 1: Si (3.5 mM) + U (VI) (0.5ppm) (no sediments and no HA)
- Batch 2: Si (3.5 mM) + U (VI) (0.5ppm) + HA (10 ppm) (no sediments)
- Batch 3: U (VI) (0.5 ppm) + HA (10ppm) (no Si and no sediments)
- Batch 4: Sediments + Si (3.5 mM) + U (VI) (0.5 ppm) (no HA)
- Batch 5: Sediments + Si (3.5 mM) + U (VI) (0.5 ppm) + HA
- Batch 6: Sediments +U (VI) (0.5 ppm) + HA (no Si)
- Batch 7: Sediments + U (VI) (0.5 ppm) (no Si and no HA)

The final volume of each sample was 20 mL, prepared in 50-mL conical tubes in triplicate. Fumed colloidal silica, silicon (IV) oxide 99%, and humic acid sodium salt (50-60% as humic acid) were obtained from Fisher Scientific. Stock solutions of humic acid (HA) and Si were prepared in deionized water (DIW) at 1000 ppm and 2000 ppm, respectively. 400 mg of sediment was weighed and placed in each tube of batches 4-7, following the addition of the respective concentrations of humic acid and silica to the appropriate batches. DI water was added up to a volume of 19 mL to leave 1 mL of volume for the pH adjustment. Once all the components were added, the concentration of uranium was injected and the pH was adjusted by using either 0.01M HCl or 0.1M NaOH. DI water was added to end up with a final volume of 20 mL. Control samples were prepared in DIW amended with U(VI) at a concentration of 0.5 ppm

U(VI), the same concentration as experimental vials, to test for U(VI) losses from the solutions due to sorption to the tube walls and caps. The samples were vortexed mixed and placed on a shaker at 100 RPM for a period of 24 hours in order to reach the adsorption equilibrium. Then, the samples were centrifuged at 2700 RPM at a temperature of 22 degrees Celsius for 30 minutes. A kinetic phosphorescence analyzer was used to measure the concentration of uranium remaining in the supernatant solution. ICP-OES was used to analyze the concentration of silica and iron in the solution. For analysis with the KPA for U(VI) and ICP-OES for Si and Fe, an aliquot was extracted from the supernatant of each test tube and diluted with 1% nitric acid between 5 to 10 times.

RESULTS AND DISCUSSION

A graphical representation of the experimental results to investigate the effect of solution constituencies on the U (VI) removal in the pH range from 3 to 8 is presented in Figure 1.

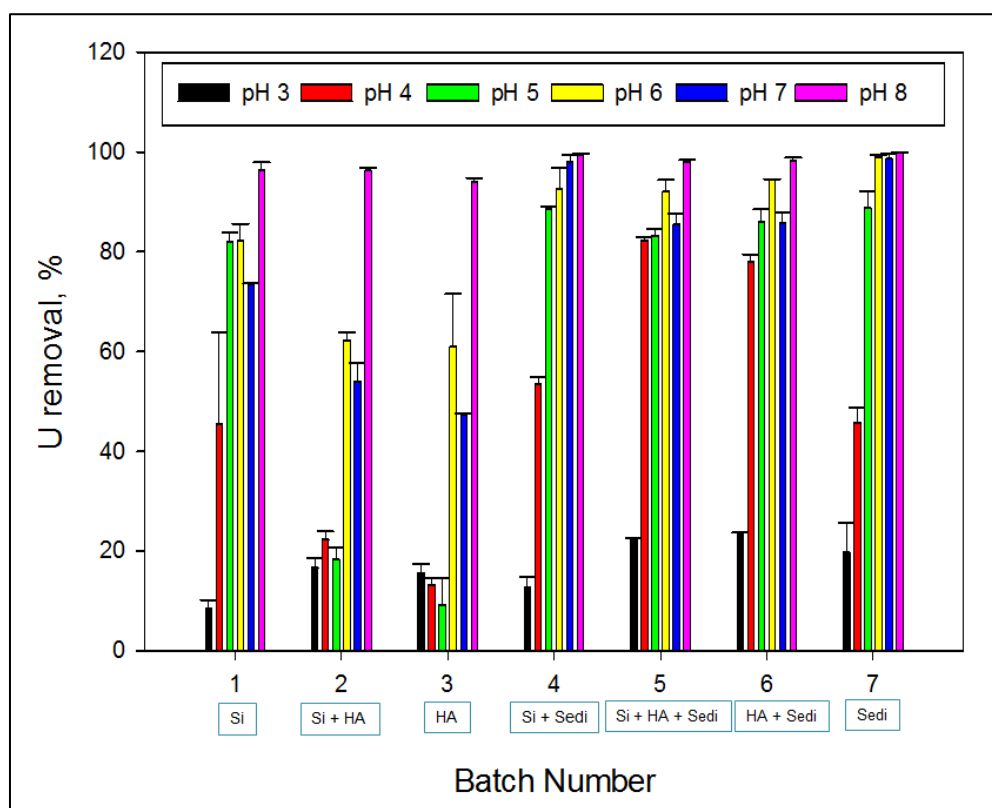


Fig. 1 Uranium removal for all batches at pH 3-8

For batch# 1, the experimental results show an increase in uranium removal with a pH increase. At low pH values, silanol groups in the silica particle are protonated, and some of them will carry positive charges. Uranium species at low pH (3-4) are in the form of uranyl cation carrying a positive charge. As pH increases, the simple uranyl cation is transformed to mononuclear and polynuclear hydrolyzed uranyl species. At equilibrium with atmospheric CO₂ the uranium speciation will be dominated by negatively charged carbonate species at pH 7 and 8.

As a result, there is very little sorption of uranium to the surface of the silica particles due to electrostatic repulsion. At pH 3 and 4, experimental data showed a removal of uranium of 8.45%

and 45.37%, respectively. Moreover, polymerization of silica is a condensation reaction that requires ionized $SiO(OH)_3^-$ groups and unionized $Si(OH)_4$. At low pH values, there are very little amounts of $SiO(OH)_3^-$ in the solution, which decreases the possibility of silica polymerization. As the pH is increased, the presence of $SiO(OH)_3^-$ groups in solution increases, resulting in a higher yield of polymerized silica. In our experiments, silica was already present in the colloidal form. The increase of pH boosts the deprotonation of the silanol groups at the surface of the formed silica particle, and this creates a net negative surface charge. Uranium species carrying positive charges dominate in the pH range from 3 to 7; so, these species can be attracted to the silica particles due to electrostatic forces. When the silanol groups at the surface of the silica particles have been neutralized by the uranium species, these particles could aggregate and precipitate out, removing uranium from the solution. The results indicate that as the pH of the solution mixture is increased, uranium removal also increases. From pH 5 to pH 8, the percentage of uranium removal is more than 80%, reaching 96.48% of removal at pH 8. Batch 1 has higher uranium removal when compared to other non-sediment batches, 2 and 3.

In batch #2, the percentage of uranium removal was noted to be reduced at pH 4, 5, 6, and 7 when the batch containing humic acid plus silica is compared to the batch containing only silica. For example, at pH 5, samples amended with silica showed 81.88% of uranium removal but samples amended with humic acid plus silica removed only 18.40%. A possible explanation is that uranium has two binding options. It can bind either to silica particles or humic acid molecules. As a result, not all the negative charges of either silica or humic acid molecules will be neutralized. Electrostatic repulsion forces are going to be stronger than any other forces, and this would substantially decrease aggregation and precipitation processes.

In batch #3, humic acid showed less efficiency in removing uranium (only 13.29% at pH 4) when compared to batch 1 (45.37%) and batch 2 (22.33%). This trend is the same at pH 5, 6, 7, and 8. In the presence of humic acid, uranyl forms uranyl-humic complexes; so, negative charges from the carboxyl groups present in the humic acid molecules will be neutralized allowing the aggregation of humic acid molecules, which are removed from the supernatant phase by centrifugation. When batch#3 is compared to batch#1 in the pH range of 4 to 8, silica shows a higher percentage of removal. Probably, silica has more sorption sites for uranium to bind than humic acid or there are more silica particles than humic acid molecules in solution. In batch #4, the percentage of uranium removal was elevated at all pH conditions when compared to non-sediment batches. Sediments provide surface sites where uranium, silica particles, or humic acid molecules can bind. The sorption of humic acid to sediment particles can change mineral surface characteristics [6]. Also, the point of zero charge (PZC) of minerals plays an important role in the uranium sorption because, below the PZC, the surface of the sediments carries a positive net charge and, above the PZC, the surface of the sediments carries a negative charge [7]. Silica (PZC = 2-3), kaolinite (PZC = 5) and goethite (PZC = 9.2) have different point of zero charge. Throughout the pH range, these minerals change surface charge from positive to negative at different pH values. In addition, sediments might have sites that more strongly bind uranium. At pH 3 and 4, the percentage of average uranium removal was found to be 12.73% and 53.42%, respectively. Apparently, the surface of the sediments carries some positive charges at low pH values, depending on the PZC of the mineral present [7]. Kaolinite and goethite present at the surface of the sediments have a net positively charge at pH 3.0-5.0, and since uranium is in the uranyl cation form at low pH values, the removal of uranium from solution is low.

Above pH 4, the uranium removal is increased to more than 88% because the surface of the sediments is getting more and more negative, attracting positive uranyl ions. According to Dong et. al. (2011), uranium sorption is dominated by goethite at high pH values, while kaolinite dominates uranium sorption at low pH values.

In batch #5, the presence of humic acid enhances the removal of uranium at pH 3 and 4, reaching a removal of 82.28% at pH 4. At pH 5, 6, 7, and 8, the presence of humic acid slightly reduces the removal of uranium when compared to batches 4, 6, and 7.

In batch #6, the results showed that the presence of humic acid molecules increases the removal of uranium (23.58%) at pH 3. At pH 4, the removal is decreased (78.10%) compared to batch 5 (82.88%). Batches 5 and 6 have the highest percentage of uranium removal at pH 3 and 4 when compared to the other batches. Above pH 4, humic acid reduces uranium sorption to sediments as can be seen when batches 4 and 7 are compared. It might be that the surface of the sediments carries a negative charge and humic acid molecules bonded to uranium are repelled because most of the carboxyl groups at the humic acid molecules also carry a negative charge.

In batch #7, at low pH values (3 and 4), sediments showed a lower percentage of uranium removal (19.85% and 45.83%, respectively) due to electrostatic repulsion because the surface of the sediments and uranium species are both positively charged. From pH 5 to 8, sediments showed the highest percentage of uranium removal (88.81-99.93%). We hypothesized that the sediments surfaces are becoming more neutral with the increase of pH; so, sediments may have more sorption sites to bind uranium than silica or humic molecules.

By comparing all the results, sediment-bearing batches showed a percentage of uranium removal higher than 80% from pH 5 to 8. In addition, in a pH range from pH 5 to 8, sediments alone performed better than when silica or humic acid were present. However, sediment amended with colloidal silica maintained increasingly higher levels of uranium removal. In the low pH values of 3 and 4, humic acid plus sediments enhanced the removal of uranium. Humic acid reduced the uranium sorption in the near neutral pH range.

CONCLUSION

To sum up, the data support the following: at $\text{pH} > 3$ some uranium sorbs to silica particles that are removed by centrifuging; the addition of humic acid lowers the amount of uranium sorbed because the humic acid does not sorb to the silica, but does form aqueous complexes with uranium; when humic acid is added to sediment it does sorb to the sediment and therefore enhances the sorption of uranium to the sediments at pH of 3 and 4.

The highest percentage of removal from the experiment was observed at pH 5 to 8 when sediments are used. Sediments offer a solid support for molecules to bind and this facilitates the removal of uranium. In the batches where only silica and humic acid are present, the percentage of removal is not high compared to the sediments because silica and humic acid molecules would have to aggregate and precipitate; otherwise, they are going to remain in solution as suspended colloidal particles. At pH values of 5-8, colloidal silica performed better for the removal of

uranium than humic acid. In future work, the concentration of humic acid will be increased to study the effects on uranium removal.

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