TECHNICAL PROGRESS REPORT

Synergy between Colloidal Si and HA on the Removal of Uranium

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Principal Investigator:

Leonel E. Lagos, Ph.D., PMP®

Florida International University Collaborators:

Yelena Katsenovich, Ph.D. Ravi Gudavalli, Ph.D. Christian Pino, DOE Fellow Alexis Smoot, DOE Fellow Sarah Bird, DOE Fellow

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Introduction

Constructed during the 1950s, the Savannah River Site (SRS) became one of the major producers of plutonium for the United States during the Cold War. Beginning with the implementation of the environmental cleanup program in 1981, SRS has become a hazardous waste management facility responsible for the storage and remediation of contaminated soil and groundwater from radionuclides. Approximately 1.8 billion gallons of acidic waste containing radionuclides and dissolved heavy metals was disposed in F/H Area seepage basins, which led to the unintentional creation of highly contaminated groundwater plumes consisting of radionuclides and chemicals with an acidic pH of 3 to 5.5. The acidity of the plumes contributes to the mobility of several constituents of concern (COC) such as tritium, uranium-238, iodine-129, and strontium-90 for the F-Area plume and tritium, strontium-90 and mercury for the H-Area plume. This investigation will focus on uranium (VI), which is a key contaminant of concern in F-Area the groundwater plume.

Initially, removal of contaminates from the polluted groundwater was implemented with a pumpand-treat and re-inject system constructed in 1997. Downgrade groundwater within the system would be pumped to the water treatment facility and re-injected upgrade within the aquifer. The effectiveness and sustainability of this process diminished over time and it was discontinued in 2004, replaced with a funnel-and-gate process. This new process would inject sodium hydroxide directly into the gates of the F-Area groundwater to effectively raise pH levels. By raising the pH of the groundwater, a treatment zone would be created by reversing the acidic nature of the contaminated sediments and producing a negative net charge on the surface of sediment particles, enhancing the adsorption of cationic contaminants. This process resulted in a decrease in concentration of Sr and U, though the concentration of iodine was unaffected by this treatment. The solution used for the injections contained a high carbonate alkalinity in order to overcome the surface acidic conditions and natural partitions in the groundwater system. To maintain the neutral pH in the treatment zone, systematic injections are required. The continuous use of high concentrations of a carbonate solution to raise pH could re-mobilize uranium previously adsorbed within the treatment zone, though this has not been observed in the monitoring data.

Humic substances (HS) are major components of soil organic matter with the ability to influence migration behavior and fate of heavy metals. Essentially, HS are polyfunctional organic macromolecules formed by the chemo-microbiological decomposition of biomass or dead organic matter. Being organic substances, HS are able to interact with both metal ions and organic compounds, and based on their solubility, HS are usually divided into three fractions (Chopping, et al. 1992). The three fractions are humin, humic acid and fulvic acid. Humin is insoluble at all pH values; HA represents the fraction which is soluble at pH greater than 3.5 and fulvic acid is soluble at all pH values.

Humic acid, which carries a large number of functional groups, provides an important function in ion exchange and as a metal complexing ligand with a high complexation capacity being able to affect the mobility of actinides in natural systems (Davis, 1982; Plancque et al., 2001). Various

studies have suggested that the retention of U(VI) via sorption in the presence of HA is a complex process due to HA forming organic coatings by sorbing on the surface of oxides and minerals, thus modifying the sorption capabilities of these metal ions (Davis, 1984; Zachara et al., 1994; Labonne-Wall et al., 1997; Perminova et al., 2002). The sorption of metal ions is considered to be enhanced at low pH and reduced at high alkaline pH (Ivanov et al., 2012). This sorption capability is also affected by the concentration of HA in the system (Chen and Wang, 2007). The U(VI) sorption onto kaolinite is influenced by the pH, U(VI) concentration, presence of inorganic carbon species and naturally occurring HA. It has also been shown that U(VI) prefers to be adsorbed onto kaolinite as a uranyl-humate complex (Krepelova et al., 2007).

This investigation will analyze any synergistic interactions between U(VI) ions, HA and colloidal silica under varying pH conditions from 3 to 8 and the presence of sediment collected from SRS FAW1. Multi-component batch systems were constructed to effectively analyze the removal behavior of U(VI).

Methodology

Removal behavior of U(VI) was studied through multi-component batch systems with a pH range from 3 to 8 in order to evaluate adsorption affected by the pH. FIU previously investigated the synergetic effect of colloidal silica and HA (10 ppm and 50 ppm) on uranium removal by preparing seven batches with various combinations of Si and HA (Lagos, et al., 2014). Expanding on this research, FIU prepared samples with 30 ppm HA to study the sorption behavior of uranium at an intermediate HA concentration. Sediment samples used in the experiments were collected at SRS from FAW1 at a depth of 70-90 feet and shipped to FIU. The sediment was sifted through a 2-mm sieve to remove gravel and larger sediment particles. Control samples were prepared in triplicate, containing deionized water (DIW) and 0.5 ppm U(VI) to account for any sorption of uranium to the container.

- Batch1: Si (3.5 mM) + U(VI) (0.5 ppm)
- Batch 2: Si (3.5 mM) + U(VI) (0.5 ppm) + HA, (no sediments)
- Batch 3: U(VI) (0.5 ppm) + HA, (no Si or sediments)
- Batch 4: Si (3.5 mM) + U(VI) (0.5 ppm) + sediments
- 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)
- Control: U(VI) (0.5 ppm), (no SI, HA, or sediments)

Fumed colloidal silica, silicon (IV) oxide 99%, and humic acid sodium salt (50-60% as humic acid) were obtained from Fisher Scientific. Stocks of HA and Si were prepared in DIW at 2000 ppm and 100 ppm, respectively. A commercial 1000 ppm uranyl nitrate stock solution in 2% nitric acid (Fisher Scientific) was used as a source of U(VI). The resulting sample mixtures were spiked with uranium to yield a concentration within a solution matrix of 0.5 ppm. Table 1 and

Table 2 present the amount of stock solutions needed to yield 50 ppm and 30 ppm of HA, respectively, with 3.5 mM of Si and 0.5 ppm of U(VI). Triplicate samples for each batch were prepared; uranium was added to each sample prior to adjusting the pH. The pH of the mixture was then adjusted to the required value using 0.01 M HCl or 0.1 M NaOH (Figure 1). Control samples were prepared in DIW amended with U(VI) at a concentration of 0.5 ppm U(VI) to test for U(VI) losses from the solutions due to sorption to the tube walls and caps. All volumes of solutions were prepared to initially have 20 mL of total volume in the sample tube. All control and experimental tubes were vortexed and then kept on the shaker at 100 rpm for 48 hours at room temperature.

	Constituents								
Batch #	SiO ₂ ml	Humic Acid ml	Uranium ml	Sediment mg	Water ml	Total Volume ml			
Batch No. 1	2.1	0	0.01	0	17.89	20			
Batch No. 2	2.1	10	0.01	0	7.89	20			
Batch No. 3	0	10	0.01	0	9.99	20			
Batch No. 4	2.1	0	0.01	400	17.89	20			
Batch No. 5	2.1	10	0.01	400	7.89	20			
Batch No. 6	0	10	0.01	400	9.99	20			
Batch No. 7	0	0	0.01	400	19.99	20			

Table 1. Experimental Matrix with Components for 50 ppm Humic Acid Experiments

D.4.1.#	Constituents									
Batch #	SiO ₂ ml	Humic Acid ml	Uranium ml	Sediment mg	Water ml	Total Volume ml				
Batch No. 1	2.1	0	0.01	0	17.89	20				
Batch No. 2	2.1	6	0.01	0	11.89	20				
Batch No. 3	0	6	0.01	0	13.99	20				
Batch No. 4	2.1	0	0.01	400	17.89	20				
Batch No. 5	2.1	6	0.01	400	11.89	20				
Batch No. 6	0	6	0.01	400	13.99	20				
Batch No. 7	0	0	0.01	400	19.99	20				

Table 2. Experimental Matrix with Components for 30 ppm Humic Acid Experiments



Figure 1. Experimental setup.

After being shaken for 48 hr at 100 rpm, the samples with 50 ppm HA were centrifuged at 2700 rpm at 22°C for 30 minutes (Figure 2). All samples, after being centrifuged, were filtered using a 0.45 µm syringe filter yielding a 3-mL aliquot. Aliquots for KPA [U(VI) analysis] and ICP-OES (Fe and Si analysis) were prepared by taking a 300-µL aliquot for KPA and a 500-µL aliquot for

ICP-OES from the filtered solutions and doing a 10x dilution with 1% HNO₃. Samples with 30 ppm HA were placed on platform shaker over a period of time until the pH of the sample was stable; pH of the samples was measured daily and readjusted with addition of an acid or base to the original pH. After the sample pH stabilized, the samples were centrifuged, following the same procedure used for the 50 ppm HA samples. Filtered and unfiltered samples were then prepared for analysis via KPA and ICP.



Figure 2. Shaker and centrifuge experimental setup.

Results and Discussion

Unfiltered samples from batches 1, 4, and 7 containing uranium, colloidal silica and/or sediment with no humic acid were analyzed using the KPA instrument; uranium removal data at different pH is shown in Figure 3. Batch 1 showed a decreasing trend starting at 60.90% removal at pH 4 to 20.97% removal at pH 8. Batch 4 also gave a decreasing trend to a lesser degree, beginning at 74.40% removal at pH 4 and 57.72% removal at pH 8. Unlike batches 1 and 4, batch 7 had a maximum removal at pH 5 (93.98%) then decreased to 65.93% at pH 8. Batch 7 yielded the highest removal among the samples, with U(VI) being able to bind to the sediment; unlike batch 4, which contains U(VI), sediment and silica and uranium could bind to silica, sediment or both. If uranium is bound to silica, it may remain in solution; this could be the reason for less removal for batch 4 and higher removal for batch 7. It might be possible that some of the U(VI) is adsorbed to the colloidal Si and cannot be measured without sample filtration. Batch 1, which only contained silica, showed significantly less removal than both batches 4 and 7. In this case, any removal would be due to silica aggregation or coagulation and positive uranyl ions present in the solution at pH 4 can interact with the negatively charged silica surface. Silica particles have a negative surface charge, the magnitude of which increases with increasing pH and increasing ionic strength (Kobayashi 2005). Krestou and Panias (2004) reported that as pH increases, the positively charged uranyl ions become negatively charged; this limits the interaction of uranium with silica particles leading to less uranium removal. Batch 1, 4 and 7 samples were filtered through a 0.45-µm syringe filter and were also analyzed via KPA to estimate uranium removal from the samples; this data is shown in Figure 4. Uranium removal for batches containing silica, batch 1 and batch 4, are in the range of 88% - 99%, while the percent of uranium removal in for batch 7 with uranium and

sediment are in the range of 75% - 99%. The higher removal of uranium in the case of filtered samples can be attributed to removal of uranium from the solution that is bound to silica, which is removed during the filtration process.



Figure 3. Uranium removal for unfiltered samples for batches 1, 4, and 7.



Figure 4. Uranium removal for filtered samples for batches 1, 4, and 7.

Batches 1, 4, and 7 containing uranium, silica and/or sediment with no humic acid were analyzed using ICP-OES in order to determine silica and iron concentrations. Unfiltered samples were analyzed; silica removal data obtained during this analysis is shown in Table 3. Batch 1 showed approximately 50% of silica removal while batch 4 data was inconsistent; most of batch 4 samples showed no detectable concentration of silica. Data obtained for filtered sample batches 1, 4, and 7 containing uranium, silica, and/or sediment with no humic acid are shown in Table 3. Batch 1 filtered samples, which contain only silica and uranium, revealed a high silica percent removal with pH 4, yielding the highest removal at 98% and subsequently decreasing until pH 8, with a removal percent of 88%. Batch 4 (silica, uranium, sediment) filtered samples had an average removal of ~97% between all pH values. Batch 7 was analyzed and revealed no silica presence, as expected; batch 7 does not contain fumed silica particles and only contains sediment and uranium; no Si release from sediment was observed.

Batch#/pH	Unfiltered	d Samples	Filtered Samples		
pH 4	Si Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	
Batch 1	54.6	7.77	97.74	2.05	
Batch 4	Not Detected	Not Detected	96.36	0.55	
Batch 7	-	-	-	-	
pH 5	Si Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	
Batch 1	55.6	1.55	96.4	1.72	
Batch 4	Not Detected	Not Detected	97.06	0.93	
Batch 7	-	-	-	-	
рН 6	Si Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	
Batch 1	48.20	4.35	92.3	1.61	
Batch 4	45.10	9.06	96.41	1.44	
Batch 7	-	-	-	-	
pH 7	Si Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	
Batch 1	51.30	6.48	88.72	3.89	
Batch 4	Not Detected	Not Detected	98.67	0.64	
Batch 7	-	-	-	-	
pH 8	Si Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	
Batch 1	41.60	2.89	88.13	2.12	
Batch 4	Not Detected	Not Detected	97.72	0.10	
Batch 7	-	-	-	-	

Table 3. Silica Removal for Unfiltered and Filtered Samples

FIU initiated synergy experiments with 30 ppm of humic acid; a fresh stock solutions of 30 ppm humic acid and 3.5 mM of silica were prepared. Triplicate samples of batches containing HA, Si, sediment and uranium were prepared by mixing a known amount of various constituents as shown in Table 4 and Table 5. Uranium was added prior to the pH adjustment and precautions were taken to add the appropriate amount of DIW so that the addition of the acid/base resulted in a total volume of approximately 20 ml. pH of the samples was adjusted with 0.01M HCl or 0.1M NaOH to the desired pH and the samples were placed on a platform shaker. The pH of the samples was measured periodically and readjusted to the original pH as needed. Table 4 and Table 5 show the data recorded during sample preparation with the amount of acid and base added to each sample. Table 6 and Table 7 show the changes in pH of the samples over time. The batches are currently being prepared for KPA analysis, and the data for pH 3 and 4 will be reported once collected.

			Constituents								
pH 3 Adjusted Set		SiO ₂	Humic Acid (HA)	Sediments	Uranium U (VI)	Vol of acid/base	DIW	p	Н		
		ml	ml	mg	ml	ml	ml	Initial	Final		
	2.1					1.80	10.50	4.35	3.03		
Batch No. 2	2.2	2.1	6	0	0.01	1.75	10.50	4.31	3.01		
1.00.2	2.3					1.80	10.45	4.52	3.03		
	3.1	0					1.60	12.75	4.12	3.03	
Batch No. 3	3.2		6	0	0.01	1.65	12.75	4.33	3.01		
11010	3.3					1.60	12.80	4.24	3.03		
	5.1					2.16	10.85	4.41	2.96		
Batch No. 5	5.2	2.1	6	400	0.01	2.23	10.60	4.18	2.97		
11010	5.3					4.39	10.60	4.30	2.98		
	6.1					3.28	12.39	4.32	2.98		
Batch No. 6	6.2	0	6	400	0.01	3.00	12.59	4.36	2.97		
190. 0	6.3					2.80	12.69	4.31	3.01		

Table 4. Sample Matrix of 30 ppm HA Batch Samples at pH 3

		Constituents											
pH 4 Adjusted Set		SiO ₂	SiO ₂ Humic Acid (HA) Sediments		Uranium U (VI) Vol of acid/base		DIW	p	Н				
		ml	ml	mg	ml	ml	ml	Initial	Final				
	2.1					1.04	11.25	4.68	4.28				
Batch No. 2	2.2	2.1	6	0	0.01	1.51	11.25	4.72	4.04				
110.2	2.3									0.23	11.25	4.56	4.03
	3.1	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			0.30	13.25	4.59	4.04					
Batch No. 3	3.2		6	0	0.01	0.20	13.25	4.51	3.88				
110.0	3.3					0.20	13.25	4.55	4.00				
	5.1					0.25	11.20	4.72	4.03				
Batch No. 5	5.2	2.1	6	400	0.01	0.25	11.20	4.66	4.00				
11010	5.3					0.23	11.20	4.59	4.06				
	6.1					0.26	13.25	5.29	4.07				
Batch No. 6	6.2	0	6	400	0.01	0.25	13.25	4.75	3.96				
110.0	6.3					0.26	13.25	4.69	4.01				

Table 5. Sample Matrix of 30 ppm HA Batch Samples at pH 4

Tabla 6	Change in	nU of Som	alog ovor	Time for	nU 2 Databag
I able 0.	Change m	ип от заш	Jies over	I IIIIe IOF	DH J Datches
	- ·· - ·				

Somple #					pН			
Salli	ipie #	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
	2.1	4.35	3.07	3.02	3.14	3.11	3.03	3.03
Batch No. 2	2.2	4.31	3.04	3.06	3.07	3.08	3.01	3.01
1100 2	2.3	4.52	2.99	3.13	3.05	3.09	3.03	3.03
	3.1	4.12	3.08	3.10	3.07	3.03	3.03	3.03
Batch No. 3	3.2	4.33	3.06	3.06	3.06	3.06	3.06	3.06
11000	3.3	4.24	3.09	3.05	3.07	3.03	3.03	3.03
	5.1	4.41	3.16	3.15	2.96	2.96	2.96	2.96
Batch No. 5	5.2	4.18	3.12	3.06	3.08	2.91	2.91	2.91
11010	5.3	4.30	3.14	2.88	3.24	2.68	2.68	2.68
	6.1	4.32	3.22	3.06	3.23	2.73	2.73	2.73
Batch	6.2	4.36	3.20	3.09	3.19	2.78	2.78	2.78
1,0,0	6.3	4.31	3.21	3.09	3.18	2.80	2.80	2.80

Somple #					pН			
Sall	ipie #	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
	2.1	4.68	4.11	4.13	4.18	4.23	4.67	4.28
Batch No. 2	2.2	4.72	9.15	4.06	4.12	4.02	4.06	4.04
1100 =	2.3	4.56	4.40	4.01	4.00	4.01	3.93	4.03
	3.1	4.59	4.30	4.05	4.01	4.17	3.99	4.04
Batch No. 3	3.2	4.51	4.24	4.04	3.98	4.04	4.07	3.98
11000	3.3	4.55	4.30	4.05	4.00	4.03	4.02	4.00
	5.1	4.72	4.13	4.07	4.05	4.02	4.03	4.03
Batch No. 5	5.2	4.66	4.21	4.05	4.04	4.02	4.00	4.00
11000	5.3	4.59	4.22	4.06	4.05	4.08	4.06	4.06
	6.1	5.29	4.03	4.03	4.07	4.11	4.07	4.07
Batch No. 6	6.2	4.75	4.18	4.06	4.11	3.96	3.96	3.96
1,5, 0	6.3	4.69	4.16	4.05	4.12	4.01	4.01	4.01

Table 7. Change in pH of Samples over Time for pH 4 Batches

Future Work

FIU will complete the experiments with 30 ppm HA batches and compare the data with the 10 ppm and 50 ppm batches on U(VI) removal. FIU will then study the effect of varying concentrations of uranium on uranium removal by changing the concentration of uranium while keeping the HA concentration constant.

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