

Synergetic Interactions between Uranium, Humic Acid, Silica Colloids and SRS Sediments at Variable pH - 16524

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ABSTRACT

The Savannah River Site (SRS) was constructed during the 1950s and became one of the major producers of plutonium for the United States during the Cold War. During its production life, the F/H Area Seepage Basins received approximately 1.8 billion gallons of acidic waste containing radionuclides and dissolved heavy metals. This led to the creation of a highly contaminated groundwater plume with uranium (VI) as a key contaminant of concern within the plume. Now, as a designated hazardous waste management facility, the main activities taking place at the site are nuclear storage and remediation of contaminated soil and groundwater from radionuclides. Humic substances (HS) are major components of soil organic matter having the ability to influence migration behavior and fate of heavy metals and are being investigated for potential use in environmental remediation at SRS. Essentially, HS are polyfunctional organic macromolecules formed by the chemo-microbiological decomposition of biomass or dead organic matter. HS are able to interact with both metal ions and organic compounds based on solubility. Humic acid (HA) represents the fraction of HS soluble at pH greater than 3.5. HA carries a large number of functional groups, provides an important function in ion exchange and is a metal complexing ligand with a high complexation capacity. Silica is the term applied to solid forms with the stoichiometric composition of SiO_2 . The colloidal silica used in this work is amorphous and nonporous in suspension; silica's net surface charge for pH values higher than 3 is negative, due to the isoelectric point being 1.5 - 2.5. Humic acid has been previously used in remediation techniques and silica is found naturally in the soil.

This investigation studied the synergistic interactions between four key components: U(VI), humic acid (HA), colloidal silica and SRS sediment under varying pH conditions ranging from 3 to 8. Multi-component batch systems were constructed to effectively analyze the removal of U(VI). The batches were pH adjusted, left to equilibrate for a minimum of 48 hours on a shaker, and then centrifuged. A set of samples, filtered to remove any colloids in suspension, and a set of unfiltered samples were analyzed. For the samples at acidic pH, the uranyl cation is the dominant species; with increasing pH, the mononuclear and polynuclear hydrolyzed uranyl ions become dominant based on speciation modeling. In filtered samples, uranium removal is highest at low pH with the negatively charged moieties of HA readily binding to the uranyl cation. Percent removal of U(VI) steadily decreased with an increase in pH and then remained comparable at a neutral/alkaline pH with the change in uranyl speciation. The percentage of colloidal silica removal was observed to be approximately 80% for both sediment- and non-sediment-bearing samples. As the pH increased, the silica removal in the non-sediment set showed a slight decrease and was in the range of 70% - 75%. Uranium removal in the unfiltered samples showed similar trends as compared to the filtered samples; however, the removal of uranium in the unfiltered samples was slightly lower compared to the filtered samples. Colloidal silica removal in non-sediment-bearing batches showed a decline with increasing pH, from 90% to

50%; conversely, the silica removal remained constant for the sediment-bearing batches at approximately 60%. Colloidal silica does not seem to have a significant effect on the removal of U(VI) before filtration due to U(VI) bound to colloidal silica remaining in suspension. The presence of humic acid, silica colloids, and SRS sediment was shown to synergistically effect the removal of U(VI).

INTRODUCTION

The Savannah River Site (SRS) began the environmental cleanup program in 1981 under the Resource Conservation and Recovery Act (RCRA). As a hazardous waste management facility, SRS is responsible for the storage of radioactive materials and remediation of soil and groundwater contaminated with radionuclides. During its production life, the F/H Area Seepage Basins received approximately 1.8 billion gallons of acidic waste containing radionuclides and dissolved heavy metals. This led to the unintentional creation of a highly contaminated groundwater plume with an acidic pH of 3-5.5. The acidity of the plume 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.

Initially, removal of contaminants from the polluted groundwater was accomplished by a pump-and-treat and re-inject system constructed in 1997. The effectiveness and sustainability of this process diminished over time and was discontinued in 2004. A funnel-and-gate process, created to replace the pump-and-treat and re-inject system, applied sodium hydroxide into the F-Area to effectively raise pH in the groundwater, creating a treatment zone; the treatment zone created reverses the acidic nature of the contaminated sediments and produces a negative charge on the surface of sediment particles, enhancing adsorption of cationic contaminants. This process effectively decreased the concentration of strontium and uranium but led to an increase in iodine concentrations. The solution used for the injections contained a high carbonate alkalinity in order to overcome the sediment's acidity in the groundwater system. To maintain the neutral pH in the treatment zone, systematic injections are required. The continuous use of high concentration carbonate solution to raise pH is of concern as re-mobilization of uranium previously adsorbed may occur.

Humic substances (HS) are major components of soil organic matter with the ability to influence absorption and migration behavior of heavy metals. HS are polyfunctional organic macromolecules formed through the chemo-microbiological decomposition of biomass or dead organic matter. Humic content of soils usually varies between 0-10% (Krepelova, 2007b). Being organic substances, HS are able to interact with both metal ions and organic compounds. The presence of humic substances in soil considerably influences the soil acidity and soil U(VI) retention properties (Crancon, et al., 2003). HS may be further divided into three fractions based on their solubility (Choppin, et al., 1992). The three fractions are: humin, which is insoluble at all pH values, fulvic acid that is soluble under all pH conditions and humic acid that is insoluble below pH 1 and soluble at pH greater than 3. All three fractions cannot be defined chemically due to each possessing a variety of functional groups arranged in non-repetitive patterns.

Humic acid plays an important role in ion exchange and, as a metal complexing ligand

with a high complexation capacity, is able to affect the mobility of actinides in natural systems (Davis, 1982; Plancque et al., 2001). HA is able to bind to both hydrophobic and hydrophilic materials due to structure and colloidal properties (Krepelova, 2007b). 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 for metal ions (David, 1984; Zachara et al., 1994; Labonne-Wall et al., 1997; Perminova et al., 2002). The sorption of metal ions is expected to be enhanced at low pH and reduced at high alkaline pH in the presence of humic acids (Ivanov et al., 2012). However, this sorption capacity is also affected by the concentration of HA in the system (Chen and Wang, 2007).

Silica is the term applied to solid forms with the stoichiometric composition of SiO_2 ; silicas vary and are well-characterized by the Si-O bond lengths, Si-O-Si bond angle and Si-O bond coordination. The surface charge of silica is negative above pH 2 (Bergna, Roberts. 2006).

Yang et al., (2013) states that SiO_2 is mainly associated with HA by weak interactions such as Van Der Waals forces and may form hydrogen bonds depending on the protonation state. Possible interactions may be occurring between the uranyl cations with the negatively charged silica.

This investigation analyzed any synergistic interactions between U(VI) ions, HA and colloidal silica under varying pH conditions from 3 to 8 in the presence of sediment collected from SRS FAW1. Multi-component batch systems were set up to effectively analyze each of these parameters and their synergistic contributions to the removal of U(VI) from the aqueous phase.

MATERIALS

Sediment samples used in the experiments were collected at SRS from FAW1 at a depth of 70-90 feet. The sediment is predominately composed of quartz, kaolinite, and goethite (Wan et al., 2011). The sediment was sieved through a 2-mm sieve to remove gravel and larger sediment particles. Fumed colloidal silica, silicon (IV) oxide 99%, and humic acid sodium salt (50-60% as humic acid, Fisher Scientific) were prepared in deionized water (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).

METHODS

Removal of U(VI) was studied through multi-component batch systems with a pH range adjusted from 3 to 8 in order to evaluate uranium removal with respect to pH. The multi-component batch systems include silica, HA, sediment, and U(VI); the batches were prepared as follows:

- Batch 1: Si (3.5 mM) + U(VI) (0.5 ppm) + HA (50 ppm), (no sediment)
- Batch 2: U(VI) (0.5 ppm) + HA (50 ppm), (no Si or sediment)
- Batch 3: Sediment + Si (3.5 mM) + U(VI) (0.5 ppm) + HA (50 ppm)
- Batch 4: Sediment + U(VI) (0.5 ppm) + HA (50 ppm), (no Si)
- Control: U(VI) (0.5 ppm), (no Si, HA, or sediment)

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 desired value using 0.01 M HCl or 0.1 M NaOH. 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 platform at 100 rpm for 48 hours at room temperature.

After 48 hours, the samples were removed from the shaker platform and centrifuged at 2700 rpm at 22°C for 30 minutes. After centrifugation, two aliquots (filtered and unfiltered) were taken; filtered samples were prepared by filtering an aliquot of supernatant solution using a 0.45 µm PTFE syringe filter and unfiltered aliquots were prepared by simply taking an aliquot of supernatant solution. Aliquots were diluted for KPA (U(VI) analysis) and ICP-OES (Fe and Si analysis) by taking a 300 µL and 500 µL of filtered and unfiltered samples, respectively, for a 1:10 dilution in 1% HNO₃.

RESULTS AND DISCUSSIONS

Triplicate samples were analyzed with KPA and ICP-OES in order to determine the uranium concentration and Si & Fe concentrations, respectively. The iron concentration was analyzed in order to ensure that no source other than the sediment was introducing Fe to the system. Further, uranium removal was calculated relative to the control.

pH 3

The percent of uranium removal for batches 1 and 2 and batches 3 and 4 at pH 3 (Table 1) ranged between 49-55% and 79-84%, respectively. Humic acid solubility is low at acidic pH while U(VI) is present as highly soluble uranyl ions (Krepelova, 2007a).

Table 1: pH 3 percent removal values for U(VI), Si, and Fe concentration

Sample-Description, pH 3	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 1 (Si, HA, U)	55.17	4.00	87.11	3.55	No Sediment	
Batch 2 (HA, U)	49.22	6.50	No Si	No Si	No Sediment	
Batch 3 (Si, HA, Sediment, U)	83.83	1.97	84.38	0.15	0.31	0.02
Batch 4 (HA, Sediment, U)	79.16	2.90	No Si	No Si	0.37	0.07

The high uranium percent removal is attributed to the competition between solubilizing HA functional groups with hydrophobic groups. At low pH, aggregation and coagulation of the HA hydrophobic groups are the major force causing complexation of uranyl cations (Tipping, 2002). Dissociation constants of acidic groups of HA were determined to be pK₁ = 3.7 ± 0.1, pK₂ = 6.6 ± 0.1 (Wang, et al., 2014). Humic acid is largely aromatic and thus insoluble when the carboxyl and other functional groups are protonated at low pH. At pH 3, the humic acid is mostly

protonated and the HA hydrophobicity becomes the dominant factor in aggregation and uranium removal; electrostatic interactions between negatively charged HA and positive uranyl cations being secondary.

Batches 1 and 2 were found to have a lower U(VI) removal compared to batches 3 and 4 with the difference being the presence of sediment. The uranium removal increased from 50% to 81% due to the presence of sediment. The sediments, due to higher surface area, are able to provide significantly more sorption sites for U(VI) and may facilitate aggregation of HA.

Silica removal percentage was found to remain similar in both batches 1 and 3, yielding $87.11 \pm 3.55\%$ and $84.38 \pm 0.15\%$, respectively.

pH 4

Uranium percent removal for pH 4 was slightly decreased for all batches compared to pH 3 (Table 2). Sediment-bearing batches still yielded an overall higher uranium removal percentage than those without sediment; a low of 40.52% without sediment compared to 70.06% with sediment. Silica removal for both batches also remained similar, yielding 82.4% and 85.61% for non-sediment-bearing batch 1 and sediment-bearing batch 3, respectively.

Table 2: pH 4 percent removal values for U(VI), Si, and Fe concentration

Sample-Description, pH 4	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 1 (Si, HA, U)	53.2	3.93	82.4	1.27	No Sediment	
Batch 2 (HA, U)	40.52	4.28	No Si	No Si	No Sediment	
Batch 3 (Si, HA, Sediment, U)	65.36	2.39	85.61	1.65	0.3	0.06
Batch 4 (HA, Sediment, U)	70.06	0.42	No Si	No Si	0.41	0.02

pH 5 and 6

At pH 5 and 6, all batches show similar results, falling within statistical error as seen in Table 3 and Table 4. For non-sediment-bearing batches 1 and 2, a gradual decrease in uranium removal was seen as pH increased; the average uranium removal at pH 3 was 53% while the average removal at pH 5 and 6 was 35% and 31%, respectively. A similar trend was observed for sediment-bearing batches 3 and 4; an average uranium removal decreased from 80% at pH 3 to 50% and 44% at pH 5 and 6, respectively.

As stated previously, pK_1 for humic acid is 3.7 ± 0.1 , resulting in HA existing predominantly in a singly deprotonated state. As seen in Table 5, below pH 5, U(VI) prevails in solution as UO_2^{2+} cations; though, at pH 5 and above, the hydrolyzed U(VI) dominates in forms such as UO_2OH^+ . Electrostatic interaction between HA and U(VI) increases at pH 5 and 6; the positive uranyl cation concentration decreases though the dominant uranium species remains positive and facilitates interaction with

deprotonated HA.

Due to increased solubility of HA as the pH increases, fewer binding sites are available for interactions. Liao et al. (2013) reported that the coordination number between U(VI) and humic acid increases from 1:1 to 1:2 when pH increased from 3 to 6. The coordination number suggests the number of ligands attached to the central ion, showing that greater amounts of HA is required to remove the same amount of U(VI).

Table 3: pH 5 percent removal values for U(VI), Si, and Fe concentration

Sample-Description, pH 5	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 1 (Si, HA, U)	38.25	3.08	85.15	3.09	No Sediment	
Batch 2 (HA, U)	32.98	4.12	No Si	No Si	No Sediment	
Batch 3 (Si, HA, Sediment, U)	49.59	1.98	85.35	0.71	0.42	0.03
Batch 4 (HA, Sediment, U)	52.18	1.43	No Si	No Si	0.48	0.02

Table 4: pH 6 percent removal values for U(VI), Si, and Fe concentration

Sample-Description, pH 6	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 1 (Si, HA, U)	30.87	5.66	77.71	4.96	No Sediment	
Batch 2 (HA, U)	32.98	5.82	No Si	No Si	No Sediment	
Batch 3 (Si, HA, Sediment, U)	43.08	0.94	84.14	1.75	0.48	0.03
Batch 4 (HA, Sediment, U)	45.82	0.84	No Si	No Si	0.59	0.07

Table 5: Uranium speciation between pH 3 and 8

pH	3	4	5	6	7	8
Uranyl Species	UO_2^{2+}	UO_2^{2+} $(UO_2)_2(OH)_2^{2+}$	$(UO_2)_3(OH)_5^+$ UO_2OH^+	$(UO_2)_3(OH)_5^+$ UO_2OH^+	$(UO_2)_3(OH)_5^+$ $(UO_2)_3(OH)_7^+$	$(UO_2)_3(OH)_8^{2-}$ $UO_2(OH)_3^-$

pH 7

The lowest overall percent removal for uranium was seen at pH 7 for all batches (Table 6). Uranium removal for non-sediment-bearing batches 1 and 2 yielded ~20%; while sediment-bearing batches 3 and 4 yielded 39.26% and 44.80%, respectively. The addition of sediment in these samples shows a ~50% increase in U(VI) removal compared to those without sediment.

Table 6: pH 7 percent removal values for U(VI), Si, and Fe concentration

Sample-Description, pH 7	U(VI) Avg Removal, %	Std.	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 1 (Si, HA, U)	19.51	3.64	75.67	4.02	No Sediment	
Batch 2 (HA, U)	20.89	1.03	No Si	No Si	No Sediment	
Batch 3 (Si, HA, Sediment, U)	39.26	1.91	84.2	0.97	0.48	0.03
Batch 4 (HA, Sediment, U)	44.80	1.66	No Si	No Si	0.68	0.18

pH 8

Uranium percent removal at pH 8 (Table 7) showed a slight increase compared to values observed at neutral pH 7. Non-sediment-bearing batches 1 and 2 resulted in a 46.14% and 34.17% removal, respectively; sediment-bearing batches 3 and 4 yielded a 41.57% and 43.52% removal, respectively. Previously, the presence of sediment showed an increase in percent removal for uranium; however, this did not hold true at pH 8. Tipping (2002) states that at high pH, the proton-binding sites of HA molecules are sufficiently dissociated to carry any significant charge, thus reducing binding potential. This is supported with the fact that pK_2 for HA is 6.6 ± 0.1 . The major species of U(VI) expected is $(UO_2)_3(OH)^{2-}$, a negatively charged complex, limiting interaction with dissociated HA.

Table 7: pH 8 percent removal values for U(VI), Si, and Fe concentration

Sample-Description, pH 8	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 1 (Si, HA, U)	46.14	2.62	68.66	4.23	No Sediment	
Batch 2 (HA, U)	34.17	5.75	No Si	No Si	No Sediment	
Batch 3 (Si, HA, Sediment, U)	41.57	0.54	83.57	0.5	0.46	0.03
Batch 4 (HA, Sediment, U)	43.52	1.34	No Si	No Si	0.58	0.03

The percent removal of uranium is directly influenced by pH, HA, silica colloids and the presence of sediment as seen in Figure 1. Interactions between these components within a system may be further explained by consideration of uranium speciation at various pH conditions. As seen in Table 5, the uranyl cation is the dominant species for uranium at acidic pH. As pH increases, the dominant species becomes mononuclear and polynuclear hydrolyzed uranyl ions. Once the pH reaches 8, the uranyl dominant species shifts from a positively charged to negatively charged polynuclear complexes.

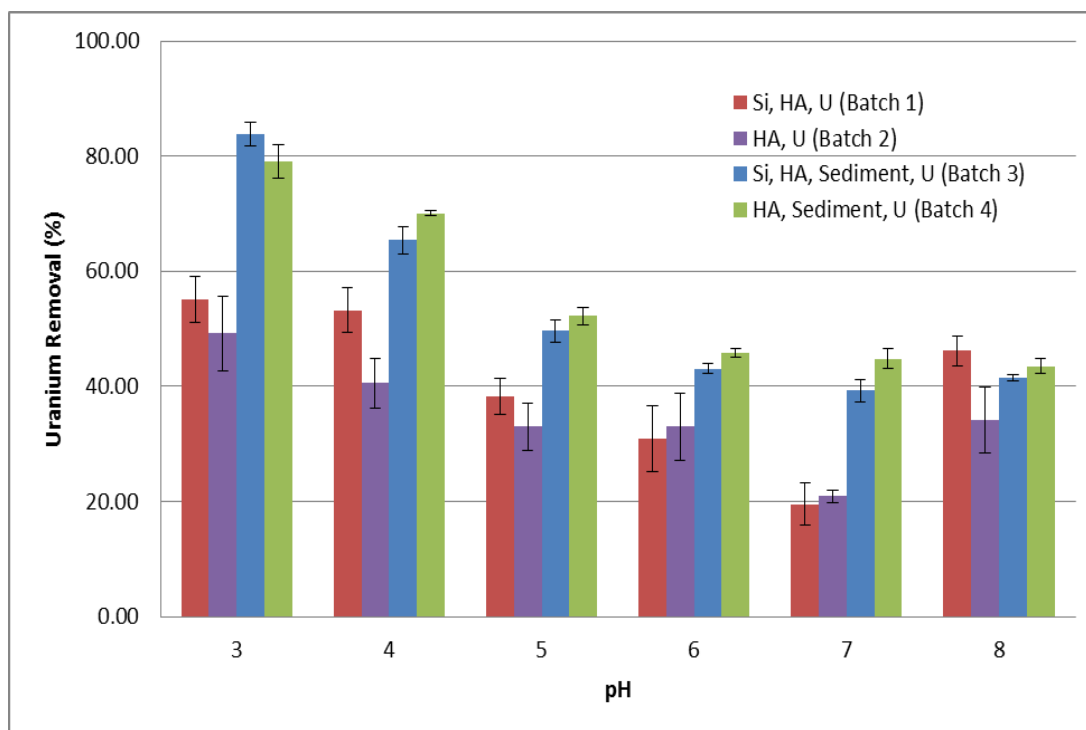


Figure 1: Uranium (VI) Removal at 50ppm Filtered between pH 3 and 8 for all batches

At pH 4.5 and below, colloidal silica particles bear little negative surface charge; so, the positively charged uranyl complexes will have little interaction (Iler, 1975). The presence of HA significantly increases uranium removal due to aggregation and, to some extent, deprotonated moieties, such as carboxylic acids, phenols and alcohols, available for interaction and binding. The addition of sediment will further increase removal by providing a larger availability of binding sites.

As pH increases from 4 towards 7, percent removal of uranium decreases as the primary species shifts from the uranyl cation to hydrolyzed uranyl complexes; reaction products may then be mixed complexes such as uranyl-hydroxo-humate. Coordination number increases (1:2), requiring more HA to remove the same amount of U(VI), unlike at acidic pH where the coordination number is 1:1.

Colloidal silica (Figure 2) removal remained similar through all pH values, though with a slight drop at pH 7 and 8. No significant effect is seen, though Koopal et al. (1998) reported that HA could rapidly and strongly absorb onto the silica surface. Filtration of samples does not affect the removal of silica other than the slight decrease noted for non-sediment-bearing samples at pH 7 and 8; the removal of silica does not seem to be affected by pH when samples are filtered, as removal remained ~80%.

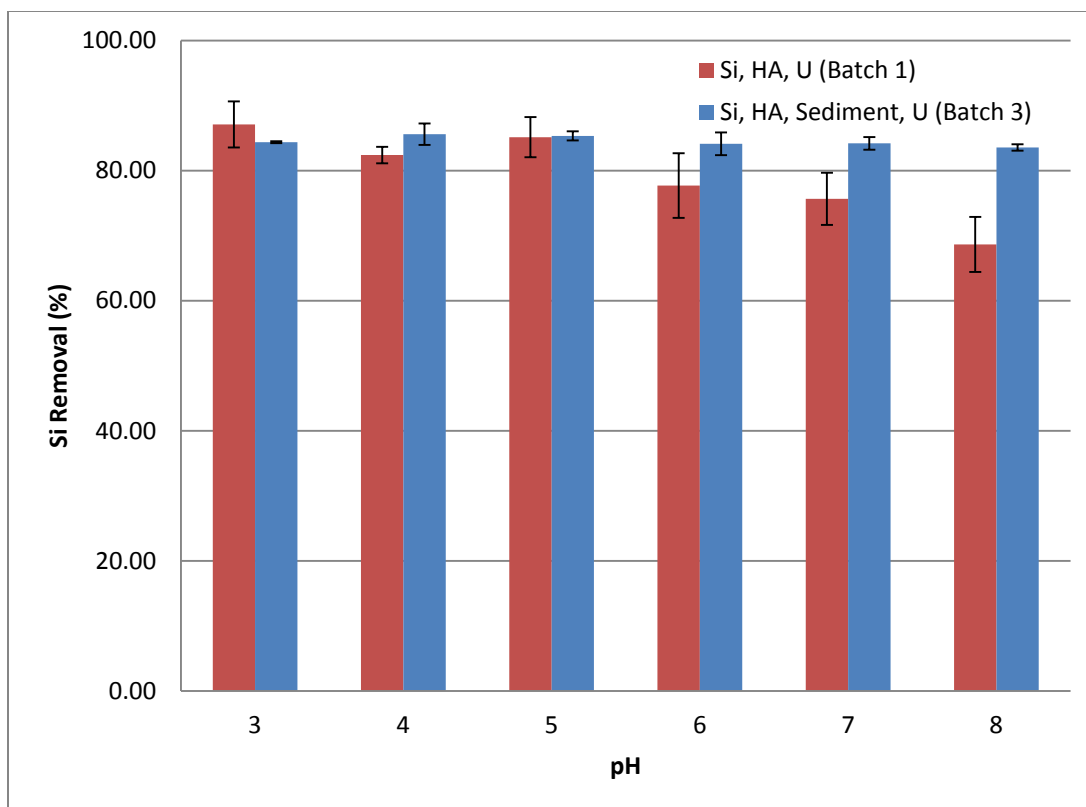


Figure 2: Silica Removal at 50ppm Filtered between pH 3 and 8 for all batches

Unfiltered Samples

The overall trend for uranium removal for the unfiltered samples remained similar to those for the filtered samples (Figure 3). The highest uranium removal occurred at acidic pH; overall uranium removal decreased as pH increased, becoming similar by pH 8. Resembling the results of the filtered samples, sediment-bearing batches 3 and 4 provided higher U(VI) removal than non-sediment-bearing batches 1 and 2. Uranium removal for sediment-bearing batch 3, containing all components (Si, HA, Sediment, U), was 71.83% at pH 3 and 33.02% at pH 8; non-sediment-bearing batch 2 revealed a 31.80% uranium removal at pH 3 and a 21.40% removal at pH 8.

Silica removal for unfiltered samples differed greatly from those of filtered samples (Figure 4). Non-sediment-bearing batch 1 gave a negative trend with the highest silica removal of 94.55% at pH 3, steadily decreasing to 44.04% removal at pH 8. Sediment-bearing batch 3 had a less substantial decrease; silica removal at pH 3 was 72.68% while being 55.71% at pH 8. Between pH 4 and 7, silica removal for sediment-bearing batch 3 remained similar, near 60%. In unfiltered samples, colloidal silica does not seem to have a significant effect on the removal of U(VI), which may be attributed to U(VI) or HA binding to silica colloids remaining in suspension. The silica may have formed semi-soluble tertiary complexes with the HA and U(VI), remaining in suspension after centrifugation though being removed once passed through the 0.45 μm PTFE filter.

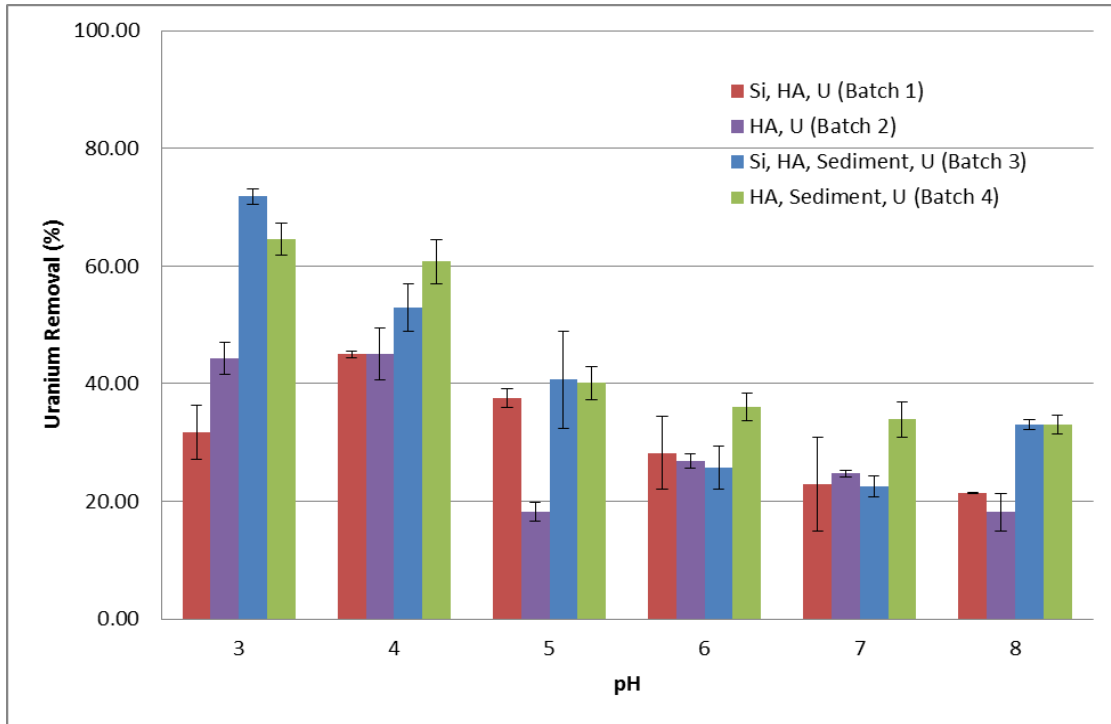


Figure 3: Uranium (VI) Removal at 50ppm Unfiltered between pH 3 and 8 for all batches

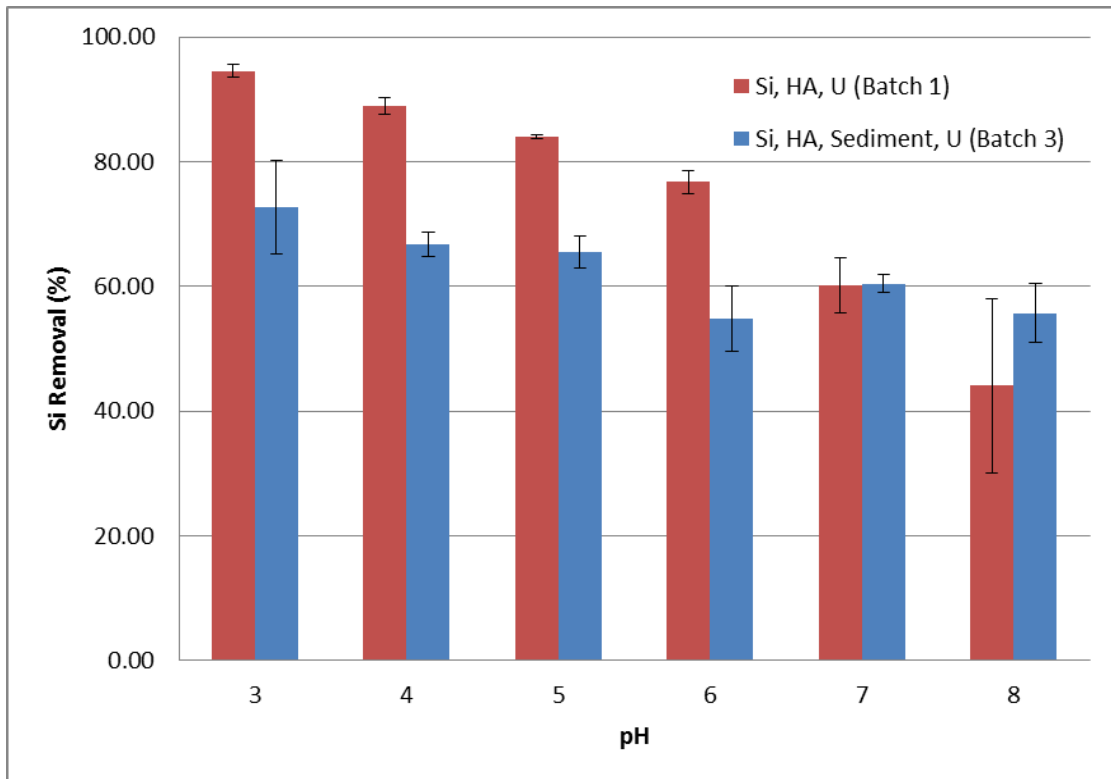


Figure 4: Silica Removal at 50ppm Unfiltered between pH 3 and 8 for all batches

Conclusion

The percent removal of uranium is directly influenced by the presence and interactions of humic acid and sediment. The natural sediment included in the samples was revealed to increase the percent removal of uranium at all pHs relative to non-sediment-bearing batches. Uranium removal at pH 3 yielded a 35% increase in the presence of sediment; as the pH reaches near neutral, the effectiveness of sediment at increasing uranium removal diminishes to 8%. Finally, colloidal silica played a minor role; any uranium removal was from a semi-soluble complex and only removed through a 0.45 μm filter. This effect is seen as silica removal after filtration averaged 80%, though non-filtered samples showed decreasing removal with non-sediment-bearing batch 1 as pH increased from 3 to 8 (94.55%-44.04%); non-filtered sediment bearing samples remained at a similar removal for all pH values of ~60%.

The multi-component batch systems revealed that synergy exists between humic acid, colloidal silica, sediment, and U(VI). Though the extent of the synergy must be further examined at other varying humic acid concentrations.

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