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## **Study of an Unrefined Humate Solution as a Possible Attenuation-based Remedy for Uranium Contamination in Acidic Groundwater - 20351**

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### **ABSTRACT**

The Savannah River Site (SRS), joined the environmental cleanup program in 1981 after the Cold War, and was designated as a hazardous waste management facility. About 1.8 billion gallons of acid wastes were disposed into the F/H Area Seepage Basin that included many radionuclides and dissolved metals, resulting in highly contaminated groundwater plumes with pH of 3 - 5.5. The acidity of the plumes contributes to the mobility of several constituents of concern (COC) such as H-3, U-238, I-129, and Sr-90 for the F-Area plume and H-3, Sr-90 and mercury for the H-Area plume. An active treatment (pump-and-treat and re-injection) system was constructed and put in place in 1997 to address the removal of metals and radionuclides from the contaminated groundwater. As remediation projects advanced, active treatments were transitioned to more passive or enhanced-passive approaches such as the subsurface barrier with base injection system, which has been controlling the mobility of contaminants. However, new and more efficient attenuation-based remedies are always sought. Several studies have proposed that humic substances can be used to remediate sites contaminated with heavy metals by creating a permeable reactive barrier. Humic substances (HS) are major components of soil organic matter. HS are polyfunctional organic macromolecules formed by the chemo-microbiological decomposition of biomass or dead organic matter. These substances are usually divided into three main fractions: humin (insoluble at all pH values), humic acid (soluble at pH greater than 3.5), and fulvic acid (soluble at all pH values). Humic substances are major components of the soil at SRS and, in addition, are also helpful in the removal process of uranium. This research focuses on uranium (VI), which is a key contaminant of concern in the F-Area groundwater plume. The interaction of uranium with sediment in the presence or absence of humic substances involves complex mechanisms that are not yet well understood. The interaction of U(VI) with humic substances can affect the adsorption of U on sediment, altering its mobility in the subsurface. The objective of this study is to study the mobility of uranium in the presence of humic acid and to determine if sediments amended by humic acid can enhance the sorption of heavy metals onto sediments.

In this research, experiments were conducted using background (clean) F-Area aquifer sediments to understand and predict uranium mobility. A blended material, humate, containing both humic and fulvic acids and a chemically modified humate (KW15 modified humics or mod-HA) was studied as a possible amendment for uranium remediation in SRS groundwater. Batch experiments were conducted in triplicates using 20 ml of aqueous suspension in DI water containing SRS sediment and mod-HA and studied the effect of pH, kinetics of humate sorption onto SRS sediment and also studied the sorption of uranium onto mod-HA amended SRS sediment. Results indicate that mod-HA amended sediment increases uranium removal significantly.

## INTRODUCTION

U.S government owned defense nuclear production facility Savannah River Site (SRS) is located 13 miles south of Aiken in South Carolina was constructed during the 1950s. During its operation, SRS produced a large amount of radioactive and hazardous acidic waste from the production of plutonium and irradiated fuel [1]. Approximately 1.8 billion gallons of acidic waste solutions containing low-level radioactivity from numerous isotopes were discharged into a series of unlined seepage basins in the F/H Area. It was believed that most of the radionuclides present in the waste solution would bind to the soil, precluding the migration of the radionuclides. The acidic nature of the plumes, however, caused mobilization of several constituents of concern (COC) such as H-3, U-238, I-129, and Sr-90 for the F-Area. Groundwater contaminated by operation of the F-Area Seepage Basins remains acidic with a pH as low as 3.2 near the basins with increasing downgradient to pH 5. The concentrations of uranium and other radionuclides exceed the Environmental Protection Agency (EPA) Maximum Contaminant Levels [2].

Pump-and-treat and re-inject system constructed in 1997 was initially used for removal of contaminants from the polluted groundwater. Downgrade groundwater within the system would be pumped to the water treatment facility and then re-injected upgrade within the aquifer. Decline in effectiveness and sustainability of this process over time resulted in discontinuation and ultimately replacement with a funnel-and-gate process in 2004. Sodium hydroxide was injected directly into the gates of the F-Area groundwater to effectively raise pH levels by creating a treatment zone reversing the acidic nature of the contaminated sediments and producing a negative net charge on the surface of sediment particles. As a result, the adsorption of cationic contaminants is expected to be enhanced. So far, this process has resulted in a decrease of Sr-90 and U-238 concentrations, though the concentration of iodine has been unaffected by this treatment. The solution used for the injections contains high carbonate alkalinity in order to overcome acidic conditions of the groundwater system. To maintain the neutral pH in the treatment zone, systematic injections are required. However, 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. HS are polyfunctional organic macromolecules formed by the chemo-microbiological decomposition of biomass or dead organic matter. These substances are usually divided into three main fractions: humin (insoluble at all pH values), humic acid (soluble at pH greater than 3.5), and fulvic acid (soluble at all pH values) [3].

Humic acid carries a large number of functional groups such as aromatic rings, carboxyl groups, phenols, aliphatic chains, etc. [4]. Humic acid is an important ion exchange and metal complexing ligand with a high complexation capacity. The ability of humic acid to chemically bind to metals influences their migration behavior and fate in natural systems [5, 6]. Various studies have suggested that the retention of U(VI) via sorption in the presence of humic acid is a complex process. For instance, humic acid can form an organic coating at the surface of minerals, which can enhance the sequestration of metals [7, 8, 9, 10]. Ivanov et al. (2012) [11] studied the sorption of U(VI) sorption onto bentonite in the presence and absence of humic acid. The study found that uranium sorption in the presence of humic acid was enhanced at low pH (below 3.8) while at moderate pH (3.8 and 6.5) uranium sorption is reduced compared to the absence of humic acid. At high pH (7 and 9), uranium sorption is reduced for both the presence and absence of humic acid [11]. Also, Krepelova et al. (2007) [12] not only found that U(VI) sorption onto kaolinite is influenced by pH, U(VI) concentration, the presence of inorganic carbon species, and humic acid but also that U(VI) prefers to be adsorbed onto kaolinite as a uranyl-humate complex [13].

A blended material, humate (HA), that contains both humic and fulvic acids is initial/raw product of an alkaline extraction of natural substances that are rich in organic matter. Based on desirable properties, various humate materials, specifically raw potassium humate (referred as Huma-K) and a chemically modified humate (KW15 modified humics or mod-HA) are being tested for remediation purposes to reduce

the mobility of uranium (VI) and other radionuclides in the subsurface at SRS. Injecting humate into the contaminated plumes augment sorption of uranium, Sr-90, I-129 by increasing ion exchange and increasing/stabilizing pH. This research focuses on batch experiments to understand the impact of mod-HA as an amendment for uranium removal.

## METHODOLOGY

### Materials

This study used sediment samples (FAW1 70-90 ft.) collected from the F-Area. This particular background sediment was selected because of similarities in mineral composition with the uranium contaminated aquifer layer. The SRS sediment was sieved (U.S. Standard Testing Sieves, Fisher Scientific), and the sediment fraction with diameter  $\leq 2$  mm was retained and used throughout the experiments. A commercial 1000 ppm uranyl nitrate stock solution in 2% nitric acid (Fisher Scientific) was used as a source of U(VI). Sorption experiments were conducted by using humate stock solution prepared by dissolving 1000 mg of mod-HA in 1000 ml of deionized water from Barnstead Nanopure Diamond Water Purification System (resistivity  $\geq 18$  M $\Omega$ ·cm). All experiments were performed under atmospheric ( $P_{CO_2} = 10^{-3.5}$ ) and ambient temperature (25°C) conditions. A blended material, humate (HA), containing both humic and fulvic acids and a chemically modified humate (KW15 modified humics or Mod-HA) was used as a humate source.

### Experimental Procedure

#### Humate Sorption Experiments on SRS Sediment

Batch sorption experiments were conducted in triplicate using 20 mL of aqueous suspension in DI water in 50 mL polypropylene centrifuge tubes, containing 1 g of SRS sediment (49 g L<sup>-1</sup>) spiked with initial mod-HA. Samples were vortex mixed for 30 sec and then rotated for 5 days on a platform shaker at 100 rpm throughout the sorption period. Equilibrate samples were centrifuged for 30 minutes at 2700 rpm, and the residual humate in the aqueous phase was measured spectrophotometrically at 254 nm using UV-Vis spectrophotometer.

Effect of pH: The effect of pH on the removal of mod-HA by SRS sediment as a result of sorption and/or precipitation was studied at a pH range of 4-8 with a reaction time of 5 days and an initial mod-HA concentration of 50 ppm. The pH was adjusted with 0.1 M HCl or 0.1 M NaOH during the reaction period. Also, control experiments using sediment-free batches of mod-HA (50 ppm) were conducted to estimate the precipitated fraction of mod-HA at pH range 4-8. The fraction attributed to sorption was calculated from the difference between the total removal and the homogeneous precipitation fraction.

Kinetics of humate removal: For the kinetic studies were conducted with mod-HA concentration of 50 ppm where humate was allowed to equilibrate with SRS sediment for different time interval of 30 minutes to 10 days at pH 4. The pH was monitored and adjusted daily by 0.1 M HCl or 0.1 M NaOH.

Equilibrium studies: For the equilibrium studies, the initial mod-HA concentration was ranged from 10-500 ppm, and the samples were reacted at pH 4 for a period of 5 days (past equilibrium time based on the kinetic study). Control experiments using sediment-free batches of mod-HA (10-500 ppm) were also conducted to estimate the precipitated fraction of mod-HA at pH 4.

#### Sorption of U(VI) Onto SRS Sediment

In order to study the sorption of uranium, SRS sediment amended with mod-HA samples were prepared by adding sediment and mod-HA into a vial and allowed to equilibrate. 200 mg of SRS sediment

spiked with a fixed mod-HA concentration of 20 ppm at constant ionic strength ( $I = 0.01 \text{ M NaClO}_4$ ) at pH 4. The samples were mixed and placed on rotary shaker for 5 days at 100 rpm. All samples were centrifuged for 30 min at 2700 rpm (Thermo Scientific Sorvall ST 16R centrifuge), and the supernatant was removed and spiked with U(VI). Samples were then mixed and placed on a platform shaker followed by centrifugation. Aqueous U(VI) concentration was measured by ICP-MS. Kinetic studies were performed by using an initial U(VI) concentration of 0.5 ppm that was allowed to equilibrate with the sediment for different time periods at pH 4. For the equilibrium studies, the initial U(VI) concentration ranged from 0.025 to 1 ppm, and samples were kept at pH 4 for a period of 7 days. The pH was adjusted with 0.1 M HCl or 0.1 M NaOH during the reaction period.

## RESULTS AND DISCUSSION

### Effect of pH on Mod-HA Sorption on SRS Sediment

Batch experiments in a pH range of 4-8 were performed in identical conditions in the presence or absence of SRS sediment to determine the percent of mod-HA removed from aqueous phase. Sediment-free samples acted as a control to provide information on humate substances precipitation with change in pH while sediment-amended samples provided total removal due to precipitation and sorption; sorption of humate was estimated from the difference between values obtained in two sets of experiment. As shown in Fig. 1, humate removal was observed to be 75% at pH 4 and then decreased to 40% with an increase in pH to pH 8. The sediment free samples prepared to study the effect of pH on precipitation of humate showed that 50% of humate precipitates at pH 4. Similar to sediment bearing samples, the humate removal due to precipitation decreases reaching 40% at pH 8. The amount of sorbed humate was calculated by subtracting the amount of precipitation from humate removal experiments at each pH value; the resulting sorption on the level of 25% at pH 4 was decreased to 0.6% at pH 8.

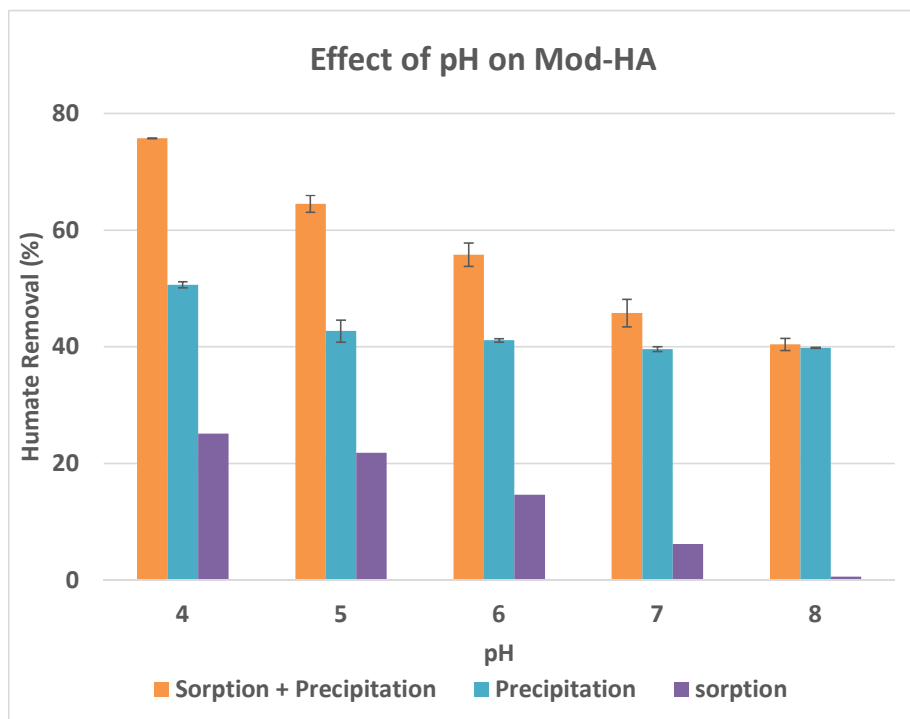


Fig. 1. Percent of mod-HA removal from aqueous phase as a function of pH

### Kinetic Studies of Humate Sorption on SRS Sediment

Kinetic studies were conducted at different time intervals (30 minutes, 1 hour, 2 hours, 4 hours, 8 hours, 24 hours, 48 hours, 72 hours, and 4 days) by preparing triplicate samples. Each sample had 1 g of SRS sediment, 50 ppm of modified humic acid (mod-HA), and 19 mL of deionized water. Samples were prepared as described in the methodology section and placed on platform shaker for the specific time. Samples were centrifuged at 2700 rpm for 30 minutes and immediately the aliquot was taken and analyzed via UV-vis for aqueous humate concentration. Humate sorption was calculated using the following equation:

$$q_t = (C_i - C_t) \frac{V}{w}$$

Where:

$q_t$  = amount of humate adsorbed to the sediments at time  $t$

$C_i$  = initial concentration of Humate

$C_t$  = concentration of Humate at any time

$V$  = total volume of solution used in the sample

$w$  = weight of SRS sediment in the sample

Fig. 2 shows the results obtained from the kinetics of humate sorption on to SRS sediments. Results indicate fast uptake of mod-HA with equilibrium reached within 24 hours.

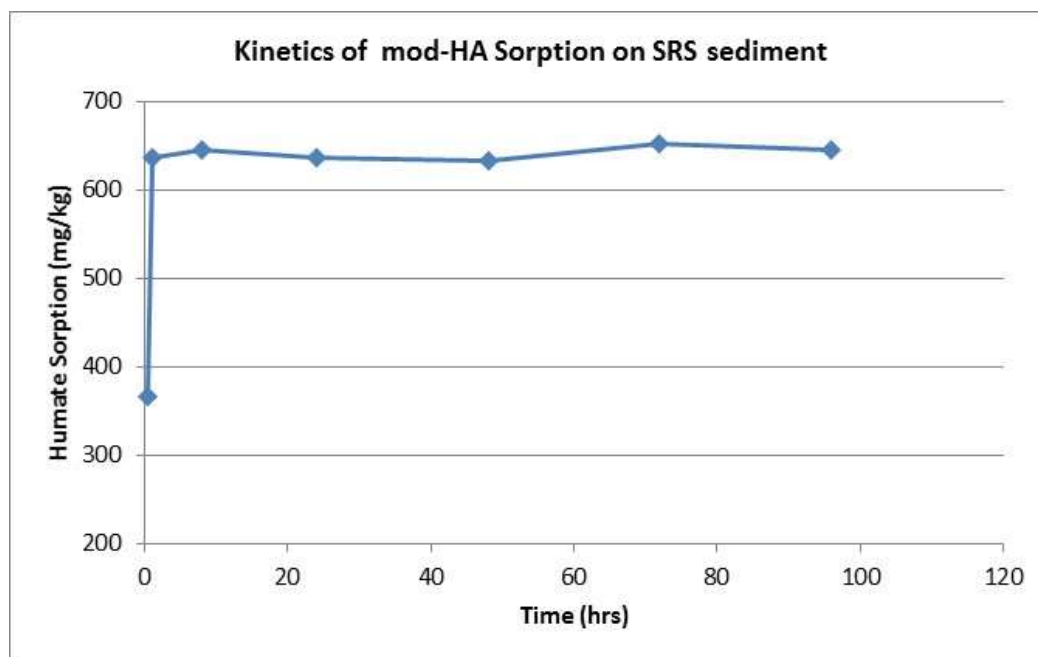
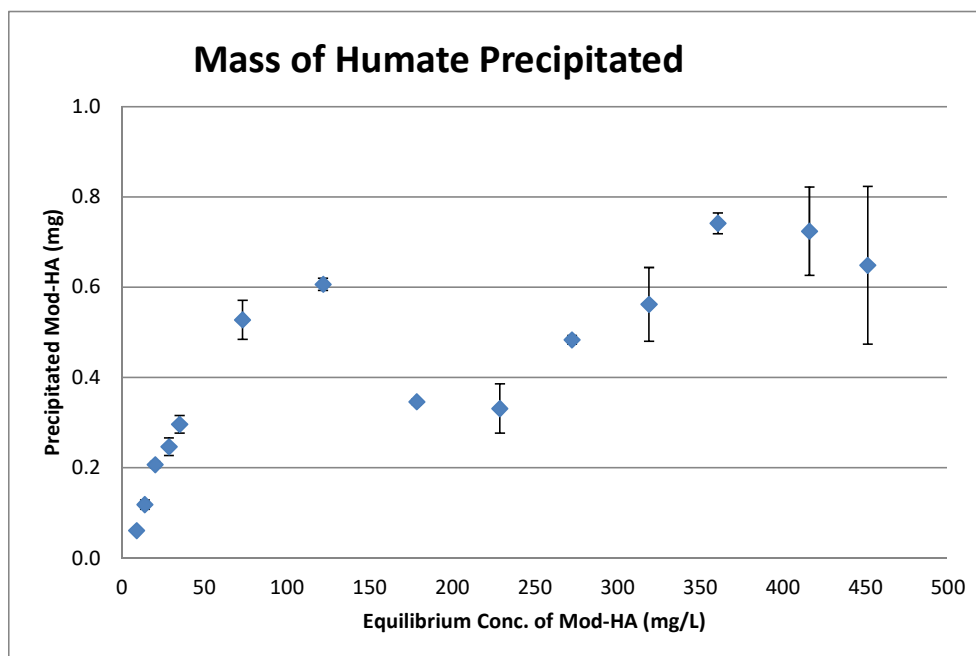


Fig. 2. Kinetics of mod-HA sorption on SRS sediment

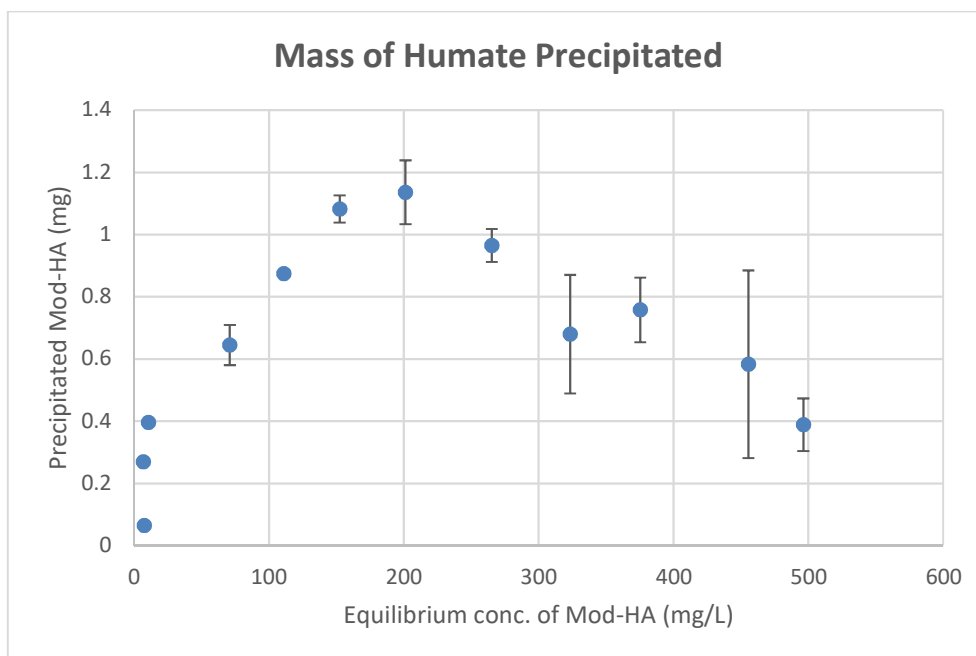
### Equilibrium Studies of Mod-HA Sorption

Control mod-HA isotherm experiment in the absence of SRS sediment was performed to determine the removal of mod-HA due to precipitation as concentration increases from 10 ppm to 500 ppm. Control sediment-free batch samples were prepared in 50-ml centrifuge tubes spiked with an appropriate amount of Mod-HA to reach the desired concentration at a pH of 4. pH of these samples was monitored and adjusted as described in the methodology section. After reaching equilibrium samples were centrifuged for 30 mins at 2700 rpm. Aqueous solution was analyzed using the UV-Vis in order to determine the mod-HA

concentrations. Fig. 3 shows that mod-HA precipitation increased with an increase in concentration until reaching 150 ppm. At this point there was a decrease in precipitation till reaching 250 ppm. Further increase in humate concentration resulted in increase in precipitation of humate. Fig. 4 shows that mod-HA removal increased with an increase in concentration until reaching 200 ppm. At this point there was a decrease in precipitation with a slight increase at around 325 ppm that drops back down on the continuous decreasing pattern.



**Fig. 3. Precipitation of mod-HA without SRS sediment**



**Fig. 4. Removal of mod-HA with SRS sediment**

### Kinetic Studies of U(VI) Sorption onto SRS Sediment with Mod-HA Amendment

Uranium sorption kinetics using SRS sediment amended with mod-HA was studied by preparing samples with 20 ppm of modified humic acid, 200 mg of SRS sediment, and 19.5 mL of DIW followed replacement of supernatant with 0.5 ppm of U(VI), and 0.1 ml of 0.01 M perchlorate and the pH adjusted to 4. Fig. 5 and Fig. 6 shows sorption of mod-HA onto SRS sediments and the kinetics of uranium sorption onto humate-coated sediment, respectively. Sorption of mod-HA was observed to be around 4500 mg/kg for the samples tested. The sorption of uranium onto mod-HA amendment SRS sediment increased sharply at 30 mins to 20 mg/kg and reached equilibrium in about 2 days with 30 mg/kg sorption. The steady state sorption of uranium onto mod-HA is similar to the sorption of uranium onto Huma-K coated sediments (not shown in the paper); however, in case of mod-HA equilibrium reached in 2 days vs 7 days in case of Huma-K.

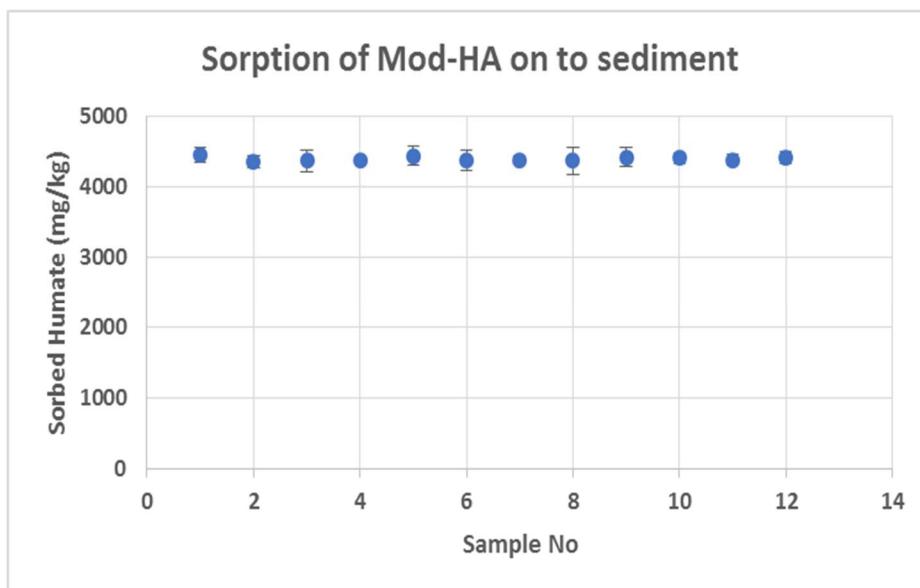


Fig. 5. Sorption of mod-HA onto SRS sediment

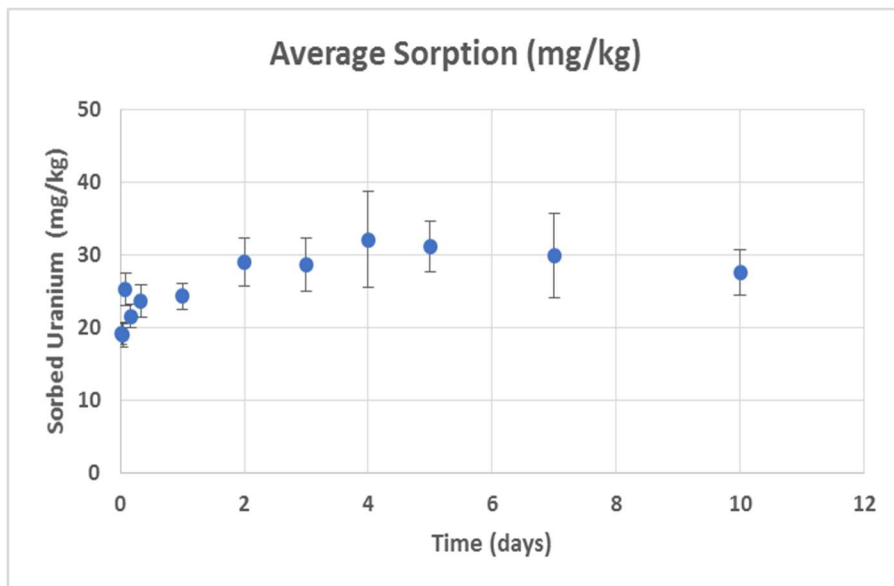


Fig. 6. Kinetics of uranium sorption onto SRS sediment amended with mod-HA



### Equilibrium Studies of U(VI) Sorption onto SRS Sediment with Mod-HA Amendment

Sorption capacity of SRS sediment amended with mod-HA was studied by conducting equilibrium studies of U(VI) sorption onto SRS sediment amended with mod-HA. Experimental data shown in Fig. revealed that the sorption of uranium increased with increase in uranium concentration measured at equilibrium conditions. Also as shown in Fig. 8, SRS sediment amended with mod-HA has a significantly higher sorption capacity compared to plain SRS sediment with similar sorption capacity to SRS sediments coated with Huma-K.

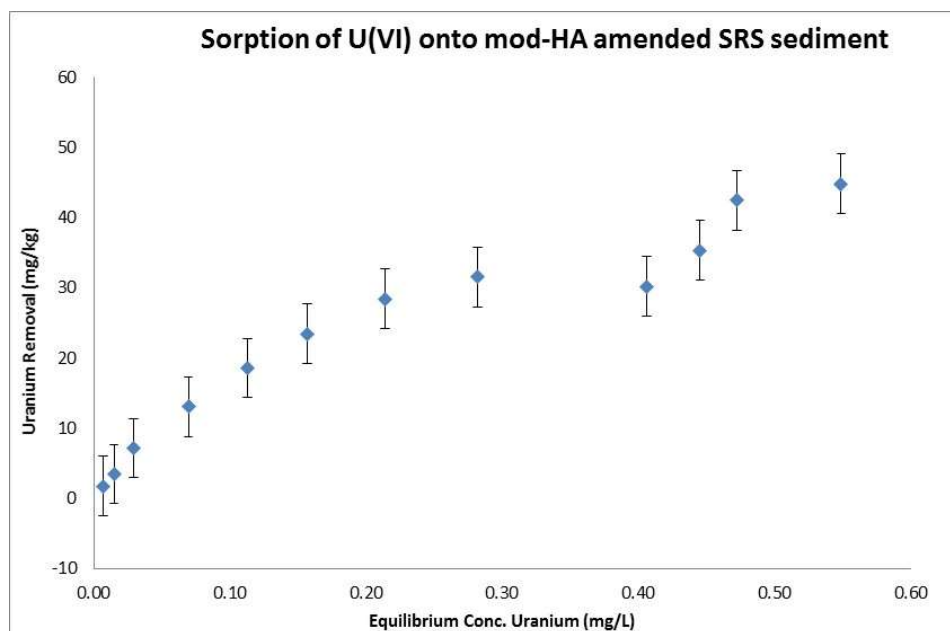


Fig. 7. Sorption isotherm of uranium on SRS sediment amended with mod-HA

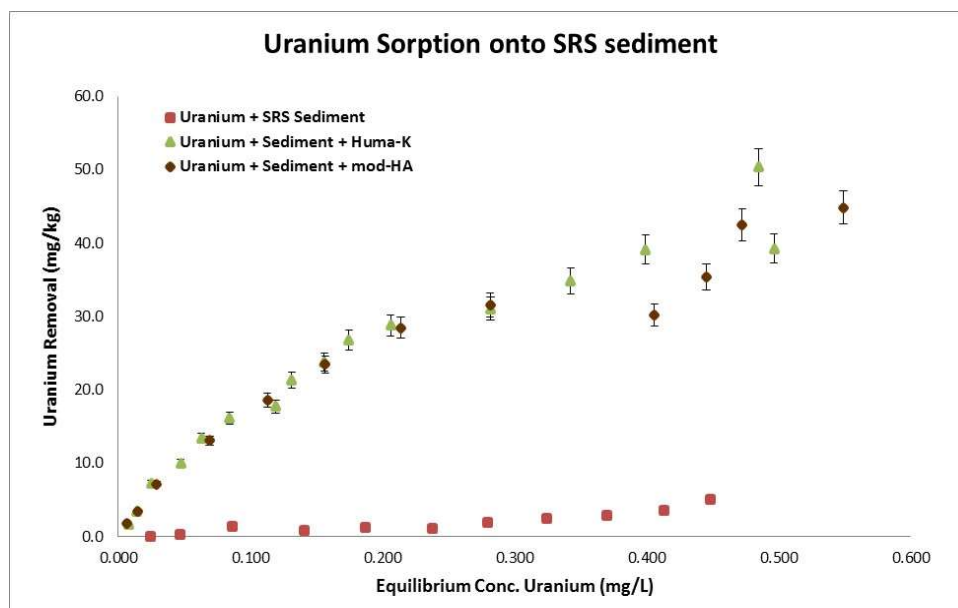


Fig. 8. Sorption isotherm of uranium on SRS sediment with and without humate amendment

## CONCLUSIONS

Overall, these experiments show proof that mod-HA amended with sediment result in an increase of uranium removal significantly. Future work will focus on to finalizing mod-HA sorption studies and to initiate desorption experiments to study effect of pH on mod-HA. Future experiments will also study the effect of pH on uranium sorption on SRS sediment coated with mod-HA.

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