

TECHNICAL PROGRESS REPORT

Progress Report on the Sorption Properties of the Humate Injected into the Subsurface System

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TABLE OF CONTENTS

TABLE OF CONTENT iii

LIST OF FIGURES iv

INTRODUCTION 1

METHODOLOGY 3

RESULTS AND DISCUSSION..... 5

FUTURE WORK 8

ACKNOWLEDGEMENT 8

REFERENCES 8

LIST OF FIGURES

Figure 1. Soil humic acid structure proposed by Schulten and Schnitzer..... 2
Figure 2. Huma-K..... 2
Figure 3. Centrifuge tube with sediment and humate solution 3
Figure 4. Shaker table with samples. 4
Figure 5. Centrifuge. 4
Figure 6. UV-Vis spectrophotometer. 5
Figure 7. Spectra of Huma-K. 6
Figure 8. Sorption experiment of Huma-K at pH 4. 7
Figure 9. Sorption experiment of Huma-K at different pH values. 7

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.

Savannah River National Laboratory has been testing an unrefined, low cost humic substance known as Huma-K as an amendment that can be injected into contaminant plumes to enhance sorption of uranium, Sr-90, and I-129. The advantage of using an unrefined humic substance is that it is inexpensive, and can thus be used for full-scale deployment of remediation technologies.

Humic substances (Figure 1) 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.

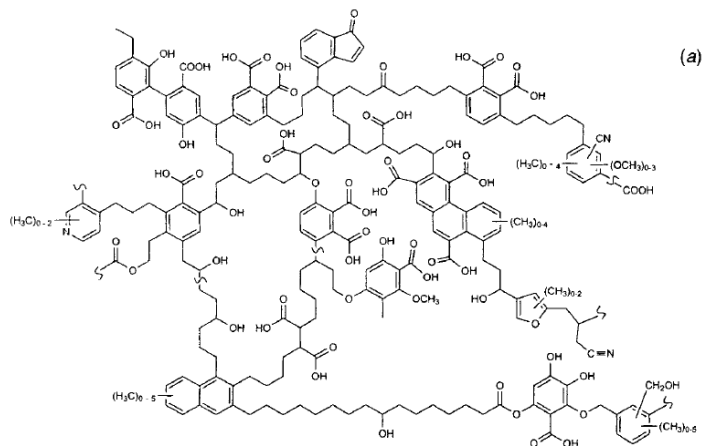


Figure 1. Soil humic acid structure proposed by Schulten and Schnitzer.

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 (Davis, 1982; Choppin, 1998; Plancque et al., 2001). pH and concentration are the main factors affecting the formation of complexes between humic molecules and metals. It is generally accepted 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 (Ivanov et al., 2012). Some studies have shown that U(VI) prefers to be adsorbed onto kaolinite as auranyl-humate complex (Krepelova, et al, 2007).

In this study, Huma-K was used, which is an organic fertilizer used by farmers to stimulate plant growth and facilitate nutrient uptake. It is a water soluble potassium salt of humic and fulvic acids that comes from the alkaline extraction of leonardite (a low-rank coal). Leonardite has a very high content of humic substances due to decomposition by microorganisms. Also, compared to other sources of humic substances, leonardite has a higher humic/fulvic acid content. The extraction of humic/fulvic acid from leonardite is performed in water with the addition of potassium hydroxide (KOH), and the resulting liquid is dried to produce the amorphous crystalline black powder/shiny flakes as seen in Figure 2.



Figure 2. Huma-K.

METHODOLOGY

Sorption Experiment of Huma-K at pH 4

In this study, Savannah River Site sediments (FAW-1 70-90ft) collected from the F-Area were used. All the experiments were done at laboratory ambient temperature (between 20 and 23 °C). A 20:1 fluid to rock ratio was used for the sorption.

First, sediments were disaggregated with a mortar and pestle using minimal force to keep the original texture of the sediment and avoid changes as much as possible. After disaggregation, each type of sediment was sieved to a particle size of ≤ 2 mm.

The sorption experiment consisted of using the same amount of sediment in the centrifuge tubes, but the concentration of humate solution was increased in order to determine the maximum sorption capability of the sediment. The following concentrations (in ppm) were used: 10, 25, 50, 100, 150, 200, 250, 300, 350, 400, 450, and 500. The final volume for all the samples was 20 ml. All the experiments were done in triplicate. First, a humate stock solution of 1000 ppm was prepared by dissolving 1000 mg in 1 liter of DI water. From this stock solution, all the concentrations were prepared.

To each centrifuge tube, 1 g of sediment was added. The corresponding humate concentration was pipetted to each centrifuge tube, and DI water was added to make a total volume of 19 ml, leaving 1 ml of volume for the pH adjustment. pH was adjusted to 4 for all the samples by using either 0.1 M HCL or 0.1 M NaOH. DI water was added to end up with a final volume of 20 ml in each tube (Figure 3).

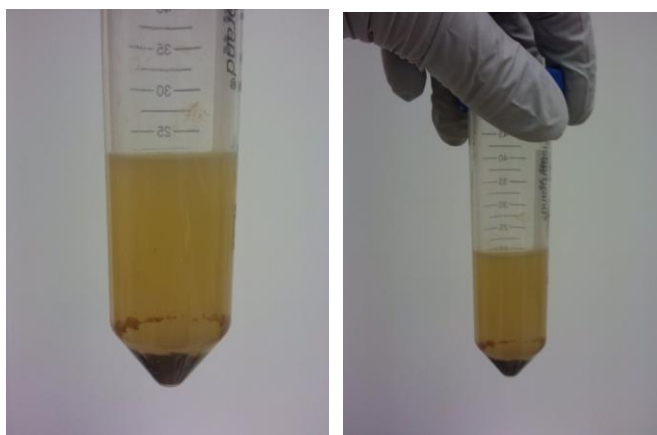


Figure 3. Centrifuge tube with sediment and humate solution.

All samples were vortex mixed and placed on a shaker table at 100 RPM for a period of 24 hours in order to reach the adsorption equilibrium. The position of the centrifuge tubes was almost horizontal in order to maximize contact between the liquid and sediment (Figure 4). Once the

samples were allowed to equilibrate for 24 hours, they were centrifuged at 2700 RPM (Figure 5) to separate the liquid solution from the sediment with the sorbed humate.



Figure 4. Shaker table with samples.



Figure 5. Centrifuge.

The liquid was analyzed using a Thermo Scientific Genesys 10S UV-Vis spectrophotometer (Figure 6). The analysis involved transferring 3 ml of the liquid sample to a quartz cuvette and placing the quartz cuvette in the spectrophotometer to measure the concentration of humate solution that was not sorbed by the sediment after equilibrium. The standard calibration curve and the measurements of the concentrations of the samples were done at a wavelength of 254 nm.



Figure 6. UV-Vis spectrophotometer.

Sorption Experiment of Huma-K at different pH values

In this experiment, a fixed concentration was used (50 ppm) to study the sorption behavior of Huma-K onto sediments at different pH values (from pH 4 to 9). The final volume for all the samples was 20 ml. All the experiments were done in triplicate.

To each centrifuge tube, 1 g of sediment was added. 50 ppm of Huma-K was pipetted to each centrifuge tube, and DI water was added to a total volume of 19 ml, leaving 1 ml of volume for the pH adjustment. pH was adjusted to the desired value for all the samples by using either 0.1 M HCL or 0.1 M NaOH. DI water was added to end up with a final volume of 20 ml in each tube.

All samples were vortex mixed and placed on a shaker table at 100 RPM for a period of 24 hours in order to reach the adsorption equilibrium. The position of the centrifuge tubes was almost horizontal in order to maximize contact between liquid and sediment (Figure 4). Once the samples were allowed to equilibrate for 24 hours, they were centrifuged at 2700 RPM (Figure 5) to separate the liquid solution from the sediment with the sorbed humate.

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RESULTS AND DISCUSSION

Before performing the experiments, the spectrum of Huma-K at different concentrations was first obtained in order to detect possible sources of interference in the measurement of concentrations using the UV-vis spectrophotometer. Figure 7 shows the spectra of Huma-K at different concentrations. It is clearly seen that interferences appear at 250 ppm and higher concentrations. The reason for this is that, at high concentrations, the distance between molecules become

smaller, and the charge distribution will be affected, which alters the molecules ability to absorb a specific wavelength. This outcome can affect the linearity of the relationship between the sample concentration and absorbance (Beer's Law). For that reason, a standard calibration curve up to 100 ppm was created. Samples that contain concentrations higher than 100 ppm will be diluted so they remain in the range of the standard calibration curve.

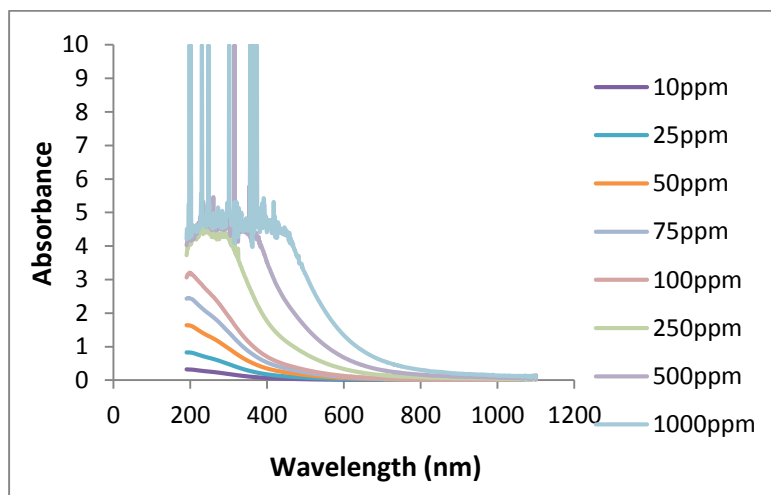


Figure 7. Spectra of Huma-K.

From the results of the sorption experiment of Huma-K at pH 4 (Figure 8), it can be seen that the sorption of Huma-K onto sediments exhibits a Langmuir isotherm up to 250 ppm. This means that a plateau is reached because all of the binding sites of the minerals surface have been occupied and no more sorption can occur. It was noticed that above 250 ppm (from 300 to 500 ppm), the sorption of Huma-K was increased. Probably there is another mechanism of interaction besides sorption between Huma-K and sediments. Since humic molecules have a hydrophobic character due to the presence of aromatic rings and aliphatic chains, at higher concentrations they will agglomerate to reduce their contact with water and settle down out of solution. Also, humic molecules can interact with the already bonded humic molecules in sediments through hydrophobic interactions, Van der Waals forces, and hydrogen bonding.

Figure 9 shows the results of the sorption experiment of Huma-K (50 ppm) at different pH values. The blue bars correspond to the total removal of Huma-K in the presence of sediments. The yellow bars correspond to the removal of Huma-K due to precipitation without sediment. The red bar is assumed to be the sorption of Huma-K calculated from the difference between total removal with sediments minus precipitation. The highest percent of Huma-K sorbed to the sediments is at pH 4 (62.8%). When the pH is increased, the sorption is decreased. At pH 7, only 6% of Huma-K is sorbed to the sediments. Beyond pH 7, there is no sorption at all. A possible explanation is that as the pH is increased, sediments become more negatively charged as well as humic molecules. The sorption is decreased due to the electrostatic repulsion between

the humic molecules and sediments. The increase of pH thus diminishes the sorption of humic molecules to the sediments. Also, whether the precipitation of Huma-K contributes to its removal was studied. The results show that at pH 4, Huma-K forms precipitates, but as the pH is increased, it becomes more soluble, decreasing the precipitation. There was minimal precipitation at pH 6 and above that pH, precipitation was not observed.

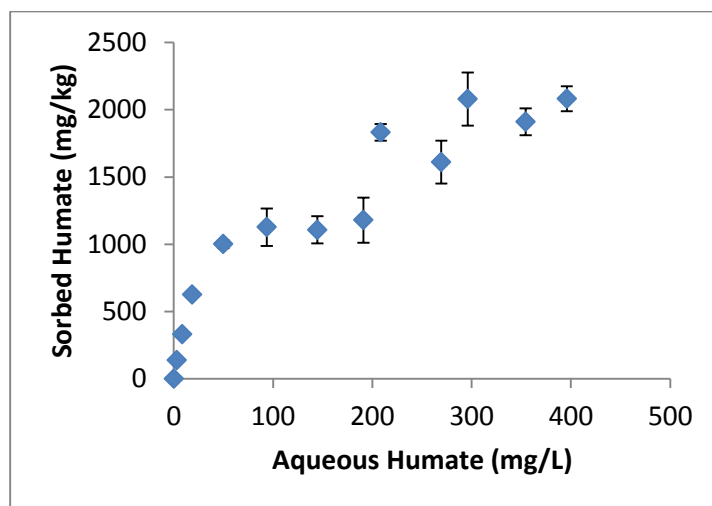


Figure 8. Sorption experiment of Huma-K at pH 4.

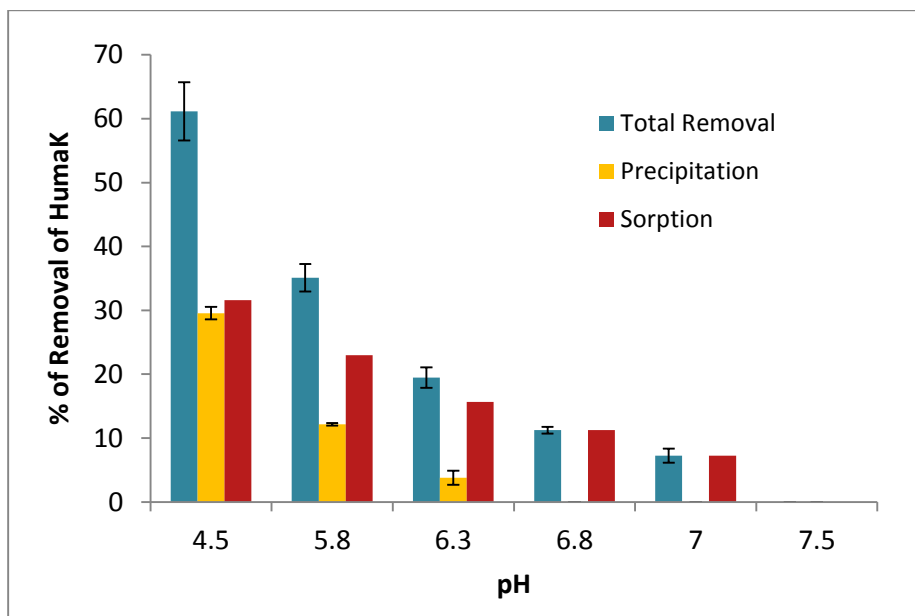


Figure 9. Sorption experiment of Huma-K at different pH values.

In summary, sorption of Huma-K onto SRS sediments apparently follows two types of sorption. First, humic molecules will occupy all the binding sites at the mineral surfaces until all are occupied. Then as the concentration is increased, humic molecules will interact with the already bonded humic molecules in the sediments and with themselves to form agglomerates and

precipitate. In the sorption of Huma-K at different pH values, it was demonstrated that the precipitation of Huma-K is increased at low pH values, and its sorption and precipitation is decreased as the pH is increased.

FUTURE WORK

Future work will focus on the kinetics study of the sorption of Huma-K at low, high, and varying pH values. Also, the desorption experiment of Huma-K with SRS sediments using the batch technique will be initiated. Once those studies are finished, FIU will proceed to include uranium using the same experimental approach in order to determine the percentage of removal using Huma-K.

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