

STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

**Study of an Unrefined Humate Solution as a
Possible Remediation Method for
Groundwater Contamination**

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ABSTRACT

A commercially available low cost unrefined humic substance known as Huma-K is being tested by the Savannah River National Laboratory as a possible amendment that could remediate heavy metal contamination in groundwater. The objective of the experiments performed during the 10 week internship was to determine if sediments amended by Huma-K could enhance sorption of metals onto sediments. Therefore, batch experiments were performed to evaluate the removal of metals with different oxidation states, including silver, zinc, and cerium, by humate amended soil at pH values of 4.5 and 6.5. These results will determine if Huma-K is suitable for remediating heavy metal contamination in groundwater at pH values in acidic and circumneutral conditions.

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1. INTRODUCTION

The Savannah River Site (SRS) was one of the major nuclear processing facilities in the U.S. where plutonium was produced during the Cold War [1]. As a result of that activity, approximately 1.8 billion gallons of acidic waste solution containing radionuclides and dissolved metals were discharged to a series of unlined seepage basins in the F-Area of SRS during 1955-1988 [2]. At that time, it was believed that most of the radionuclides present in the waste solutions would not migrate to groundwater due to the binding with soil. This was true for some radionuclides, but several uranium isotopes, ^{129}I , ^{99}Tc , and tritium migrated into the groundwater, creating an acidic plume with a pH between 3 and 5.5. For many years, efforts have been made by the Department of Energy to clean up the site and remediate the groundwater. Groundwater contaminated by operation of the F-Area Seepage Basins remains acidic with a pH as low as 3.2 near the basins and increasing downgradient to 5, and has concentrations of U (VI) and other radionuclides that exceed the Environmental Protection Agency (EPA) designated Maximum Contaminant Levels [3]. The 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 and other heavy metals by sediment. The advantage of using an unrefined humic substance is that it is inexpensive and can 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 [4]. 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 [5]. Humic substances are divided into three main fractions: humic acid (HA), fulvic acid (FA), and humin [6]. Their size, molecular weight, elemental composition, structure, and the number and position of functional groups vary. These substances have functional groups such as carboxylic acids, alcohols, sulfates, and amides among others that can interact with metals forming humic-metal complexes. Therefore, it is possible that metals can interact with soil that has been amended with humic substances.

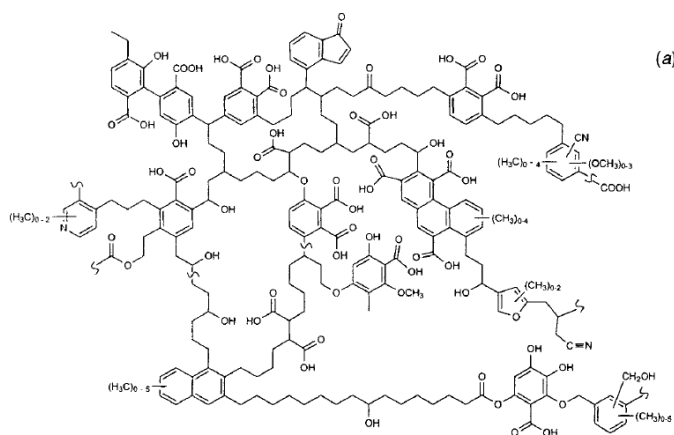


Figure 1. Soil humic acid structure proposed by Schulten and Schnitzer.

This study evaluated the sorption of metals with different oxidation states, silver, Ag(I), zinc, Zn (II), and cerium, Ce(III), at two different pH values (4.5 and 6.5) by soil amended with Huma-K. These three metals were chosen for this study to have a better understanding on how metals with different oxidation state interact with soil amended with Huma-K. In addition, these metals are found in trace amount in Huma-K and it is unlikely that these low concentrations will have a significant effect on the results compared to the higher concentrations of other metals present in unrefined Huma-K material. Huma-K 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.

The objective of this internship research was to determine if the low cost unrefined humate solution known as Huma-K can be used to enhance the sorption of metals on humate amended soil. This study can assist in evaluating whether Huma-K can be used as an *in situ* amendment for the remediation of groundwater contaminated with different metals and if it can be implemented at other DOE sites.

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2016, a DOE Fellow intern Hansell Gonzalez Raymat spent 10 weeks doing a summer internship at Savannah River National Laboratory located in Aiken, South Carolina, under the supervision and guidance of Dr. Miles Denham. The intern's project was initiated on June 4, 2016, and continued through August 13, 2016 with the objective of studying the removal of different metals by Huma-K.

3. RESEARCH DESCRIPTION

3.1 Sorption of Huma-K onto SRS sediments

For the sorption experiment, a Huma-K stock solution of 1000 mg L^{-1} was prepared by dissolving 1000 mg of Huma-K in 1 L of 0.01M NaNO_3 . SRS sediments were sieved to a particle size of less than 2 mm. Batch sorption experiments were conducted by bringing 1 g of SRS soil in contact with 20 mL of Huma-K solution. The initial Huma-K concentration was in the range $10\text{-}400 \text{ mg L}^{-1}$ at both pH 4.5 and 6.5 at constant ionic strength (0.01M NaNO_3). Samples were homogenized by vortex mix for 30 seconds. The samples were placed on a platform shaker (100 RPM) to ensure homogeneous suspension contact throughout the sorption period (three days). pH was monitored and adjusted as necessary daily. After three days, all the samples were centrifuged for 30 minutes at 2700 RPM, and the supernatant was measured spectrophotometrically at 254 nm (Thermo Scientific Genesys 10S). All the experiments were done in triplicate.

3.2 Sorption of Ag^+ , Zn^{2+} , and Ce^{3+} onto SRS sediments

For the metal sorption experiment, stock solutions of the metal ions were prepared as follows: for Ag, Zn, and Ce, 0.0318 g of AgNO_3 , 0.0975 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 0.061 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water to produce solutions with a concentration of 1000 mg L^{-1} . Batch sorption experiments were conducted by bringing 1 g of SRS soil in contact with deionized water spiked with initial metal concentrations of $C_0 = 0.25, 0.5, 1, 2, \text{ and } 4 \text{ mg L}^{-1}$ at pH 4.5 and 6.5 and constant ionic strength (0.01M NaNO_3). The samples were vortex mixed, placed on a platform shaker for three days, and centrifuged. The supernatant was analyzed by inductively coupled plasma emission spectroscopy (ICP-ES).

3.3 Sorption of Ag^+ , Zn^{2+} , and Ce^{3+} onto SRS sediments amended with Huma-K

Initially, 20 mL of Huma-K solution with a fixed concentration (200 mg L^{-1}) at pH 4.5 and 6.5 was brought in contact with 1 g of SRS soil for three days. After three days, the samples were centrifuged and the supernatant was replaced by deionized water (ionic strength 0.01M NaNO_3) at pH 4.5 and 6.5. Samples were left to be equilibrated on the platform shaker and centrifuged in the same way as previously explained. This process was performed twice. After two desorption steps, the supernatant was replaced by deionized water spiked with initial metal concentrations of $C_0 = 0.25, 0.5, 1, 2, \text{ and } 4 \text{ mg L}^{-1}$ at pH 4.5 and 6.5 and constant ionic strength (0.01M NaNO_3). Samples were vortex mixed, placed on a platform shaker, and centrifuged. The supernatant was analyzed by ICP-ES.

3.4 Sorption competition of Ag^+ , Zn^{2+} , and Ce^{3+} onto SRS sediments amended with Huma-K

These experiments followed the same procedures explained in section 3.3 but instead of a single element, a mixture of three metals in the solution was used to perform sorption experiments. After two desorption steps, the supernatant was replaced by deionized water (ionic strength 0.01M NaNO_3) spiked with initial metal concentrations $C_0 = 0.25, 0.5, 1, 2, \text{ and } 4 \text{ mg L}^{-1}$

following by pH adjustment at pH 4.5 and 6.5. The samples were vortex mixed, placed on a platform shaker for three days, and then centrifuged. The supernatant was analyzed by ICP-ES.

4. RESULTS AND ANALYSIS

4.1 Sediment characterization

The sediments that were used for the batch experiments were characterized by Brunauer-Emmett-Teller (BET) N₂-specific surface area and X-ray diffraction analysis. The BET data showed that the sediments have a specific surface area of 4.29 m²/g. The X-ray diffraction (XRD) analysis (Figure 3) revealed that the sediments are composed predominantly of quartz and kaolinite. Further studies will be done to analyze the fine fraction in order to detect by XRD iron mineral phases.

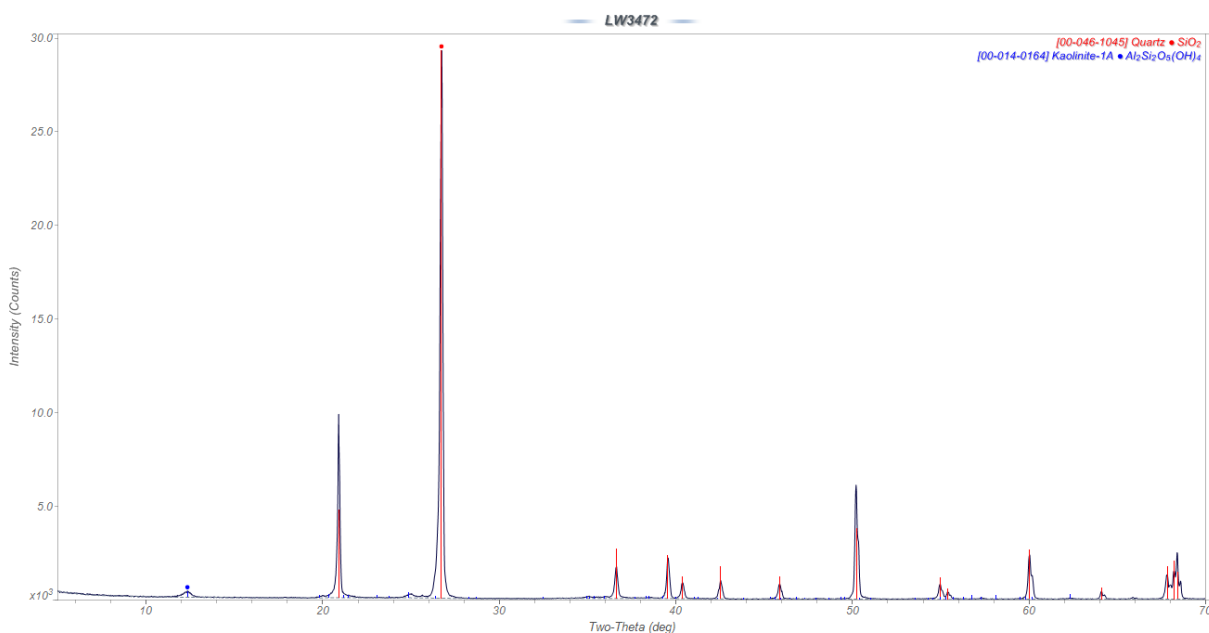


Figure 3. X-ray diffraction of SRS sediments.

4.2 Sorption of Huma-K onto SRS sediments

The equilibrium studies between Huma-K and SRS soil with an initial Huma-K concentration between 10-400 mg L⁻¹ at pH 4.5 and 6.5 for a period of three days (Figure 4) showed that sorption of Huma-K onto SRS sediments reaches a plateau at C₀ = 200 mg L⁻¹ at both pH values. As the concentration of Huma-K is increased, its sorption onto the sediments stays practically the same meaning that all of the binding sites in the SRS sediment have been occupied, following a typical Langmuir type behavior. Also, the decrease of surface charge of humic substances in Huma-K by the low pH (pH 4.5) and its hydrophobic moiety allow these humic molecules to have a higher sorption at pH 4.5 on the SRS sediment surface compared to the sorption at pH 6.5. pH has an effect on the sorption of humic substances, which tends to decrease with the increase of pH. The reason for this is that as the pH is increased, the deprotonation of the functional groups such as carboxylic acid groups in humic substances increases, and this results

in an increase in the negative charges of humic substances that will cause electrostatic repulsion from the surface of the SRS sediments. Also, the decrease in the adsorption at pH 6.5 compared to 4.5 indicates that the adsorption may result from the interactions with positively charged surface sites of the sediments. Most likely, humic substances in Huma-K interact with kaolinite (identified by X-ray diffraction analysis) where the binding mechanism between humic substances and hydroxyl groups on the surface of kaolinite minerals in the sediments is believed to be through ligand exchange, where the $-OH_2^+$ and $-OH$ groups at the surface are exchanged with the anionic groups such as carboxyl groups in the humic substances [7-9]. As the pH is increased, fewer $-OH_2^+$ and $-OH$ groups are going to be available for the binding of humic substances due to the deprotonation; therefore, adsorption is decreased as can be seen for the sorption at pH 6.5.

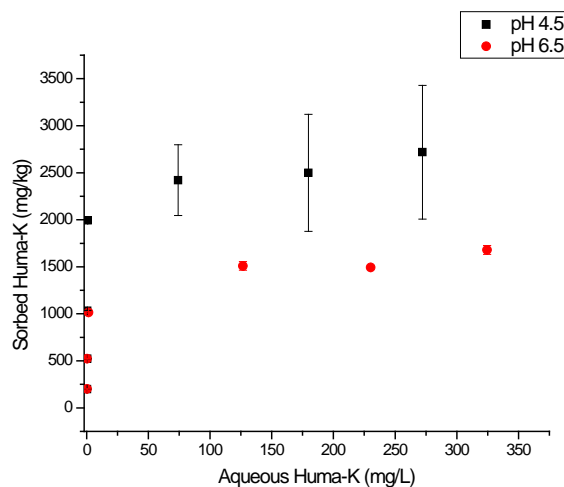


Figure 4. Sorption isotherm of Huma-K.

4.3 Desorption of Huma-K

A desorption study between Huma-K and SRS sediments was conducted at a pH 4.5 and 6.5 (Figure 5). The results show that at pH 4.5, the desorption of Huma-K after two events is not high compared to the desorption at pH 6.5 which was significantly higher. A possible explanation for this behavior is that at low pH values there is no increase in negative charges in humic substances or the surface charge of sediments that could stimulate the desorption process. Mostly, humic molecules that have a weak interaction with sediments (either physical or reversible adsorption) are desorbed easier. At higher pH values such as 6.5, humic molecules and sediments tend to be more negatively charged due to the deprotonation of the carboxyl groups and other functional groups. This effect leads not only to mutual repulsion of humic molecules adsorbed on the surface enhancing the desorption but also an increase in their solubilization [10].

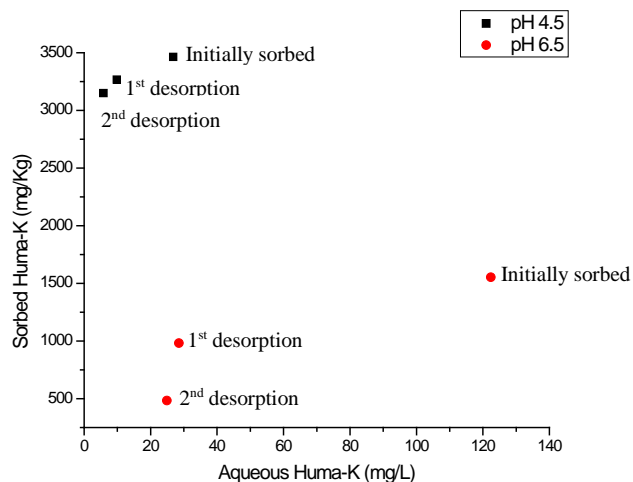


Figure 5. Desorption of Huma-K.

4.4 Sorption of Ag^+ , Zn^{2+} , and Ce^{3+} onto SRS sediments and SRS sediments amended with Huma-K

Humic substances coated on the surface of the sediments can enhance the complexation properties of the sediments for the removal of metals in groundwater by providing additional complexation sites compared to the existing ones at the sediments' surface. The degree of enhancement provided by the humic-rich layer of the sediments depends on pH and stability constants between humic substances and metals. As can be seen in Figure 6, the sorption of the three metal cations (Ag, Zn, and Ce) was higher at pH 6.5 compared to pH 4.5 for both SRS sediments with and without Huma-K coating. The reason for the increase in sorption of metals with the increase in pH is that sediment particles are electrically charged, and as the pH is increased, the surface of the sediments become negatively charged, resulting in a metal cation attraction towards the surface of the sediments. In other words, sorption of metal cations takes place on surfaces of opposite charge but little on surfaces of neutral or similar charge. In comparison to SRS sediments without Huma-K, sediments amended with Huma-K showed an enhancement in the sorption at both pH values for Zn and Ce but not for Ag. The reason for this is that humic molecules become negatively charged as the pH is increased due to the deprotonation of its functional groups (carboxyl groups), providing more complexation sites for the sorption of metals, which results in an enhancement in the sorption of Zn and Ce. In addition, electrostatic repulsions between ionized groups in the molecular structure of humic substances makes them adopt a more expanded configuration, making binding sites more accessible to the metal cations. Although for Ce, sediments without Huma-K coating performed slightly better than the sediments coated with Huma-K at pH 6.5. It was noted that for Ag, there was not an enhancement in the sorption by sediments amended by Huma-K due to Ag has a weak hydrolysis behavior and a low stability bond with oxygen electron donors [11]. In fact, a speciation modeling software (Medusa-Hydra) was used to confirm that none of the metals (Ag, Zn, and Ce) are dominated by hydroxyl complexes under the experimental conditions. Therefore, sediments amended with Huma-K did not improve the removal of Ag. Probably, the sorption of Ag onto sediments occurs only through sorption onto iron hydroxides [12].

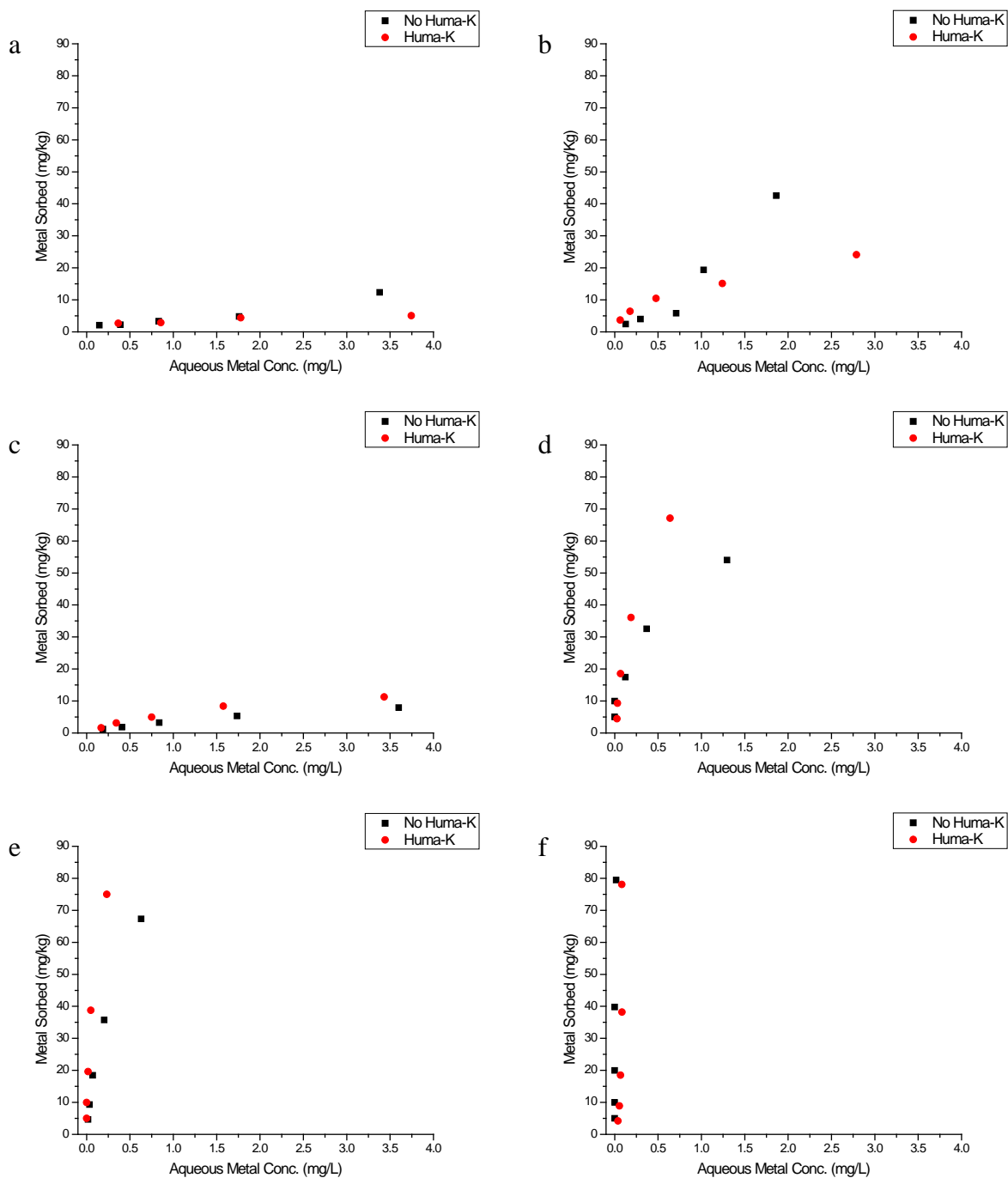


Figure 6. Sorption of Silver, Zinc, and Cerium onto sediments amended with and without Huma-K: (a) Silver pH 4.5, (b) Silver pH 6.5, (c) Zinc pH 4.5, (d) Zinc pH 6.5, (e) Cerium pH 4.5, and (f) Cerium pH 6.5.

4.5 Sorption competition of Ag⁺, Zn²⁺, and Ce³⁺ onto SRS sediments amended with Huma-K

The experimental data for the sorption competition between Ag, Zn, and Ce (spiked as a mixture at the same time) onto SRS amended with Huma-K is shown in Figure 7. It was found that sorption of the three metals increased with pH from 4.5 to 6.5. Also, it was found that Ce had a higher sorption compared to Ag and Zn at both pH values. When the results of the sorption competition of Ag, Zn, and Ce spiked as a mixture at the same time in the same sample were compared with the sorption of Ag, Zn, and Ce spiked individually in separate samples (Figure 8), the comparison showed that the data points for the three metals almost overlap. This means that there is no sorption competition between Ag, Zn, and Ce. The reason for that is some metals do not compete for the same binding sites. This experiment serves as a confirmation that Ag, Zn, and Ce do not compete for the same binding sites.

Silver is a type-B metal cation meaning that it tends to coordinate and form complexes with soft bases, having a high affinity for sulfur [13]. The stability constant of Ag with carboxylate complexes ($K = 10^2 - 10^4$) is lower than the stability constant with organosulfur complexes ($K = 10^{13}$) [14]. It is expected that Ag will not compete for the binding sites with Ce or Zn because its affinity is towards functional groups that contain sulfur donor ligands. Some studies have shown that organic matter present in soil increases the sorption of Ag, probably due to its complexation with sulfur groups [15-17]. In this study, Huma-K did not show any significant increase in sorption because humic substances with increasing maturity (humification process) tend to lose functional groups. Also, the least abundant functional groups in humic substances are the ones containing sulfur, resulting in few binding sites for the complexation of silver [5]. Zinc is on the borderline between soft acids and hard bases according to the Pearson's HSAB classification system. This means that it will have intermediate properties of both hard and soft acids having no strong preference for hard over soft bases. For that reason, in the sorption experiments, Zn has a higher sorption compared to Ag. Complexation studies between Zn and humic acid have shown that zinc forms weak complexes compared to other divalent metal cations [18]; therefore, it will not displace Ce which forms stronger complexes with humic substances. Cerium is classified as a hard acid, so it will most likely interact with hard bases such as carboxylate (RCOO^-) and hydroxyl (OH^-) groups. This greatly favors the interaction between humic substances and Ce because the most abundant functional groups in humic substances are carboxylate groups resulting in an enhancement in the removal of Ce from the aqueous solution as can be seen by the results obtained in this study. Also, this means that the binding sites for Ce are different than the binding sites for Ag because first is a hard acid and the other one is a soft acid. In addition, it has been reported that the stability constants ($K = 10^5 - 10^6$) for the complexation of Ce with humic acid is strong [19].

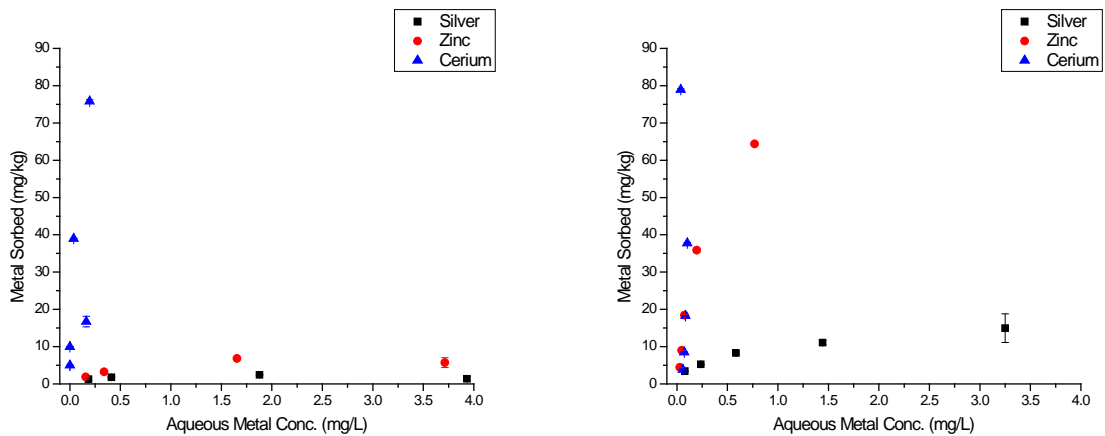


Figure 7. Sorption competition between Ag, Zn, and Ce (spiked as a mixture at the same time) onto sediments amended with Huma-K at pH 4.5 (right) and 6.5 (left).

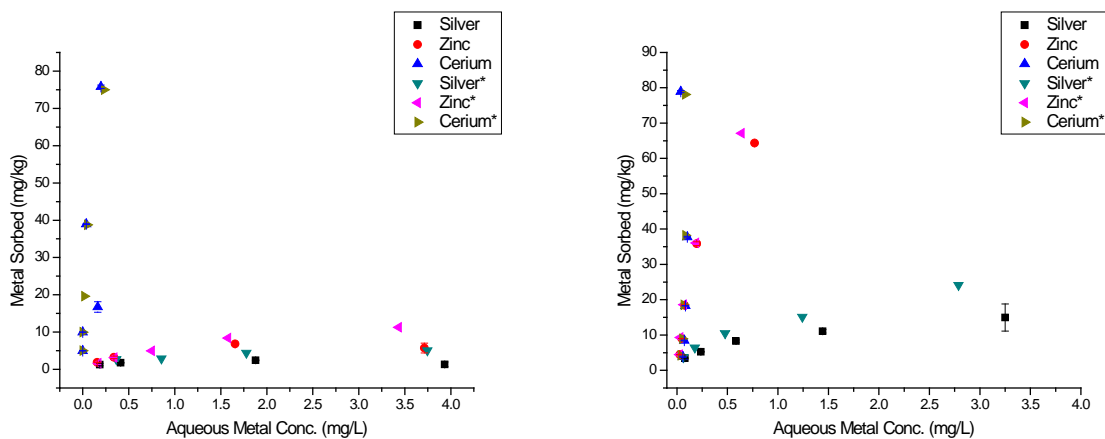


Figure 8. Comparison of sorption competition (Ag, Zn, and Ce spiked as a mixture at the same time) with individual sorption of Ag*, Zn*, and Ce* on sediments amended with Huma-K at pH 4.5 (right) and 6.5 (left).

5. CONCLUSION

Based on this study, it can be concluded that the application of Huma-K to remediate contaminated soil is a promising remediation method. It can be used to amend sediments to enhance the removal of some metals from aqueous solution at acidic and circumneutral solutions. Sorption experiments of Huma-K onto SRS sediments showed that pH affects the sorption of Huma-K by decreasing sorption with an increase of pH. The Huma-K desorption from sediment was found lower at pH 4.5 compared to pH 6.5; at this pH conditions there was a fraction of humic substances still sorbed to the sediments. Sediments amended with Huma-K performed better in the removal of Zn and Ce compared to sediments without Huma-K amendment and the removal of these metals at pH 6.5 was noted higher. As for silver, sediments amended with Huma-K did not show any sorption enhancement, probably due to the lack of surface functional groups where silver tends to interact. In addition, it was found that there was no binding competition between Ag, Zn, and Ce because they may interact with different functional groups on the surface of sediments and Huma-K.

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