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

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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ABSTRACT

Unrefined, low cost humic substances are being tested by Savannah River National Lab as a possible amendment that could remediate groundwater contaminated by an acidic plume by sorption of contaminants such as Uranium, Sr-90, and I-129 onto sediments. The objective of the experiments performed during the 10 week internship was to understand how an unrefined humic substance sorbs to aquifer sediments when injected; what is the maximum loading capacity of the sediments; how much is desorbed; and what fraction of humic molecules sorb to the sediments. A UV-vis spectrophotometer was used for the measurement of the concentration. E_4/E_6 and E_{ET}/E_{BZ} ratios will provide information about molecular weight and degree of substitution of the humic molecules. This information is useful for planning a strategy for full scale deployment of a groundwater remediation technology at Savannah River Site.

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1. INTRODUCTION

Savannah River Site (SRS) was one of the major nuclear processing facilities in the U.S. where plutonium was produced during the Cold War. As a result of this 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 the SRS during 1955-1988. At that time, it was believed that most of the radionuclides present in the waste solution would bind to the soil and would not migrate. This was true, but sufficient 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. SRS groundwater 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.

Savannah River National Lab 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 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 in to 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.
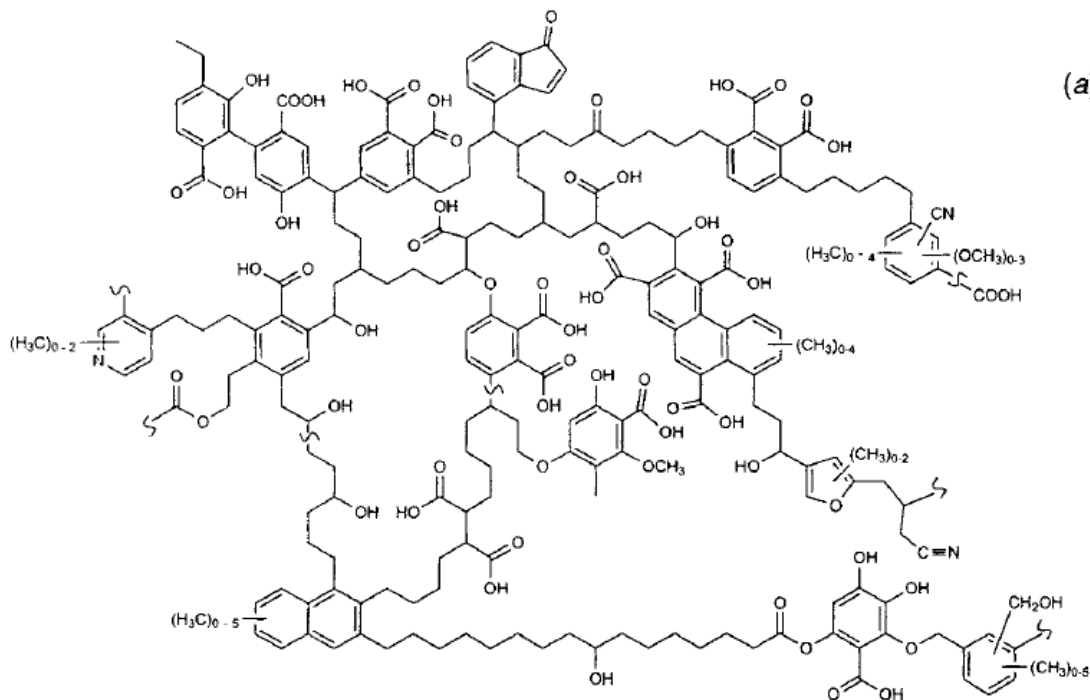
Figure 1. Soil humic acid structure proposed by Schulten and Schnitzer.

In this study, Huma-K was used, which is an organic fertilizer used by farmers to stimulate plant growth and facilitates 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 these experiments is to study how Huma-K sorbs to aquifer sediments when it is injected, in order to understand its sorption behavior; the maximum sorption loading capacity of humate on sediments; and how much it fractionates by molecular weight when sorbing or desorbing. This study can assist in evaluating whether Huma-K can be used as an in situ amendment for the remediation of groundwater contaminated with uranium.

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Development Program, 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 2014, 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 May 31, 2014 and continued through August 9, 2014. The intern focused on conducting batch experiments to study the sorption and desorption behavior of low cost humate known as Huma-K which is an agricultural product. Four types of sediment were used in the experiments in order to study the loading capacity of the sediment, and the possibility of any desorption of the humate sorbed to the sediment.

3. RESEARCH DESCRIPTION

Adsorption Experiment of Huma-K Using Four Types of Sediment at pH 4

In this study, four types of sediment from the SRS F-area were used. Sediment FAW-1 90-91ft (B1) and sediment FAW-1 94-95ft (B2) are from an uncontaminated area. Sediments FAW-5E 59' (B3) and FAW-5G (B4) are from a contaminated area that was exposed to the acidic plume. The sediments used in this experiment were collected and stored at room temperature in a core facility. 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 and desorption experiments.

First, the four types of sediment were disaggregated with a mortar and pestle using minimal force to keep the original texture of the sediment and avoid as little changes as possible. After disaggregation, each type of sediment was sieved to a particle size of ≤ 2 mm. Each type of sediment was carefully homogenized by using a soil splitter (Figure 3).

Figure 3. Soil splitter.

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 four types of sediment. For the sediments B3 and B4, the following concentrations (in ppm) were used: 35, 40, 45, 50, 100, 150, 200, 250, and 300. For B1 the concentrations (in ppm) used were: 1, 5, 10, 25, 30, 35, 50, 100, 150, 200, 250, 300, 350, and 400. For B2 the concentrations (in ppm) used were: 25, 30, 35, 50, 100, 150, 200, 250, 300, 350, and 400. The final volume for all the samples was 20ml. All the experiments were done in triplicates. 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, 1g of sediment was added. The corresponding humate concentration was pipetted to each centrifuge tube, and DI water was added up to a total volume of 19 ml to leave 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 4).
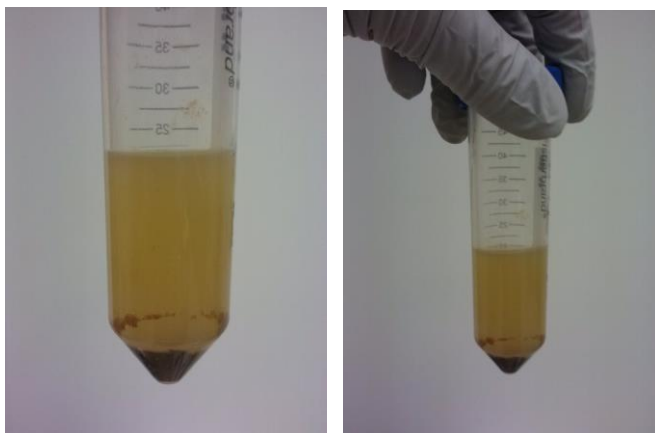
Figure 4. Centrifuge tube with sediment and humate solution.

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 liquid and sediment (Figure 5). Once the samples were allowed to equilibrate for 24 hours, they were centrifuged at 2700 RPM (Figure 6) to separate the liquid solution from the sediment with the sorbed humate.
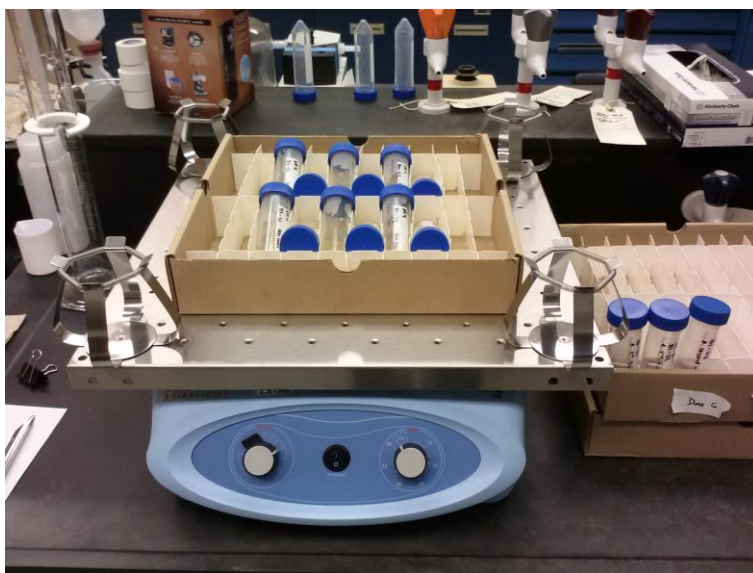
Figure 5. Shaker table with samples.

Figure 6. Centrifuge.

The liquid was analyzed using a Thermo Scientific Genesys 10S UV-Vis spectrophotometer (Figure 7). 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 450 nm.
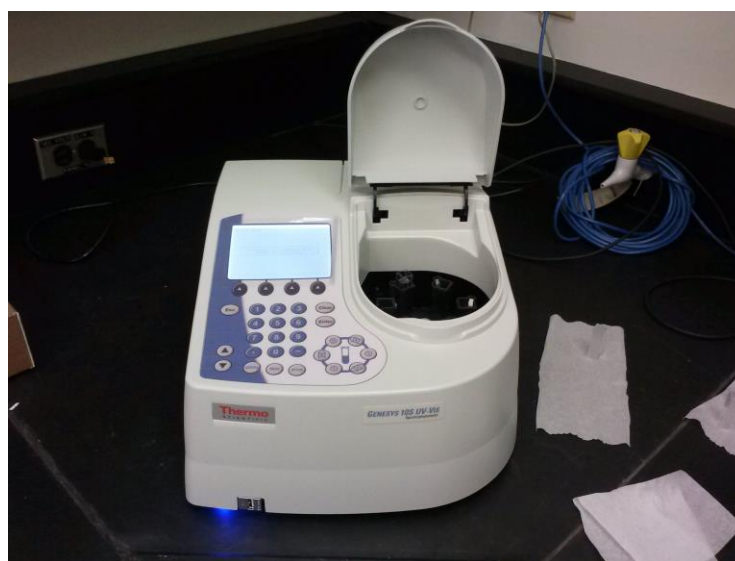
Figure 7. UV-Vis spectrophotometer.

Desorption Experiment of Huma-K using four types of sediment at pH 4

In this study, the liquid from each sample for the four types of sediment was removed as much as possible, and it was replaced by adding DI water at pH 4 from the stock solution to a final volume of 20 ml (DI water stock solution at pH 4 was prepared by adding 0.1M HCL to DI water). 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 equilibrium. The position of the centrifuge tubes was almost horizontal in order to maximize contact between liquid and sediment (Figure 5). Once the samples were allowed to equilibrate for 24 hours, they were centrifuged at 2700 RPM (Figure 6) to separate the liquid and the solid phase. The concentration of humate desorbed from the sediment for all the samples was measured by analyzing the liquid using a UV-Vis spectrophotometer at wavelength 450 nm. Also, the E_4/E_6 ratio (ratio between the absorbance at 465 nm and 665 nm) and the E_{Et}/E_{Bz} ratio (ratio of absorbance at 253 nm and 220 nm) was measured using the UV-Vis spectrophotometer. This desorption process and analysis was done four times only for the 300 ppm sample of each sediment, and once for the rest of the concentrations.

4. RESULTS AND ANALYSIS

The first step in the study was the determination of a wavelength suitable for the measurement of the concentration of the humate solution. Huma-K standard solutions were scanned from 190 nm to 1100 nm in the UV-vis spectrophotometer. As seen in Figure 8, the spectra of Huma-K standard solutions have a featureless character where the absorbance of the humic substances decreases as the wavelength is increased. The high absorbance of light in the UV region (190-380 nm) is due to the presence of chromophores (functional groups such as aromatic rings, carboxylic acids, phenols, and aliphatic chains) that absorb light at specific wavelengths to excite electrons from the ground state energy level to a higher energy level. There is no definite peak where it reaches maximum absorbance, therefore the wavelength 450 nm was chosen for measurement of the concentrations. The reason for choosing this wavelength is that it has been used in other papers for the measurement of concentration of humic substances in solution.
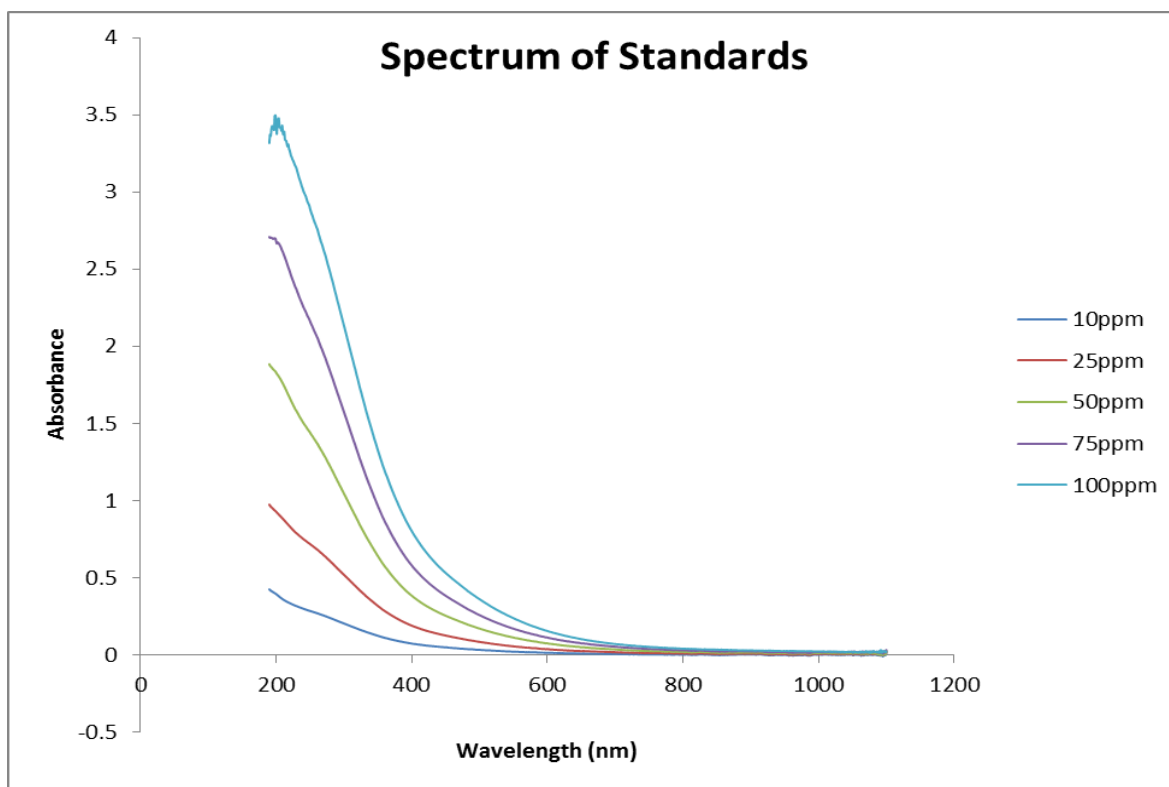

Figure 8. Spectra of standards.

Adsorption Experiment of Huma-K using four types of sediment at pH 4

The adsorption experiments are best described by using isotherms. An adsorption isotherm is a curve that relates the concentration of a solute in the liquid C_e (mg/L) to the concentration of the solute on the surface of an adsorbent Qe (mg/kg) at a constant temperature. From this type of isotherm, the sorption behavior, maximum sorption capacity, and interaction between the adsorbent and adsorbate can be determined. Figure 9 below shows the plots for the four types of sediment, where the amount of humate sorbed to the sediment is plotted against the humate remaining in solution as the humate concentration is increased. Sediment FAW-1 90-91ft (B1) and sediment FAW-1 94-95ft (B2) were collected from an uncontaminated area. Sediment FAW-5E 59' (B3) and sediment FAW-5G (B4) are from a contaminated area that was exposed to the acidic plume. It was known from previous analyses that sediments B2 and B4 had higher clay contents than B1 and B3. The clay contents of the particular samples used in this study are currently being quantified by SRNL.
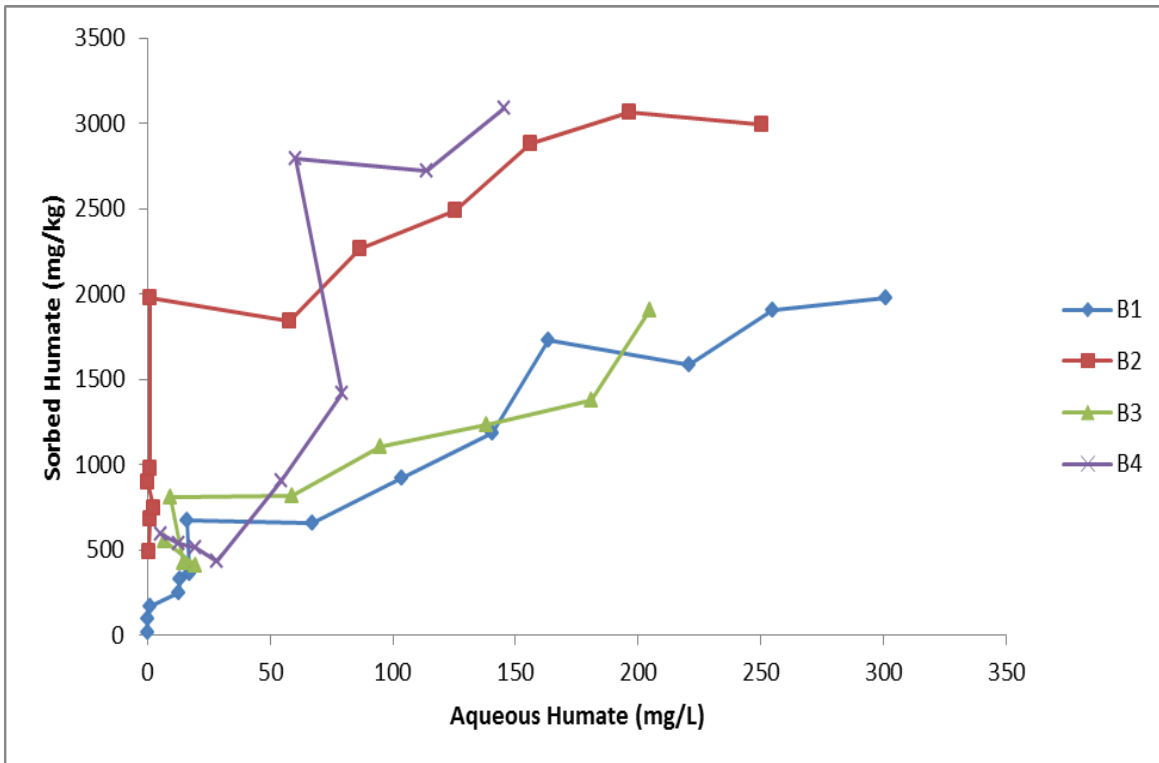
Figure 9. Adsorption Isotherm for the four types of sediment.

From the plot in Figure 9, the sediments that show higher adsorption are B2 and B4, followed by B1 and B3. B1 and B2 come from the same sampling site where B1 was collected at 90-91 ft and B2 was collected at 94-95 ft, yet they have different sorption capacities for humate. The explanation for the difference in sorption for the four types of sediment is that different sediments have different numbers of sorption sites affecting the sorption of the humate. In addition, mineral composition is an important factor in the sorption of the humate to the sediments because different minerals have different points

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of zero charge. If the pH is below the point of zero charge, hydroxyl groups at the surface of the minerals are protonated carrying a positive charge. If the pH is above the point of zero charge, hydroxyl groups are deprotonated carrying a negative charge. Sorption of humate to the sediments at pH 4 is favored if the minerals have a positive charge because at this pH, carboxyl groups present in the humic substances of the humate solution possess a negative charge and will be attracted to the minerals through electrostatic attraction. If the minerals possess a negative charge, then humic substances will not bind to the minerals due to the electrostatic repulsion. The mechanism of sorption of the humic substances to the sediments is through electrostatic and hydrophobic interactions. Humic substances that have high molecular weight, high content of aromatic rings, and high content of aliphatic chains will bind to the humic molecules already bound to the sediment creating layers and layers of bound humic molecules in order to decrease interactions with water molecules.

Form the plot in Figure 9, apparently B2 and B4 at pH 4 show higher sorption capacity of humate because B2 and B4 have higher clay contents, providing more sorption sites for humic molecules to bind. Also, mineral composition for B2 and B4 favors the sorption of humate. The decrease in sorption of humate in the sediments B1 and B3 may be due to less sorption sites for humic molecules to bind, and possibly mineral composition. Also, B1 and B2 show that a plateau is reached as the concentration of humate is increased, meaning that no more humate will bind to the sediment. In the case of B3, it seems that a plateau is reached, but higher concentrations have to be tested with this particular type of sediment in order to see if the plateau is formed. B4 does not show any plateau which probably means that saturation of the surface with humate was not reached, and testing of higher concentrations of humate is needed.

The data from the adsorption experiment was used to test the Langmuir and Freundlich models. These models can predict the partitioning behavior between sediment and humate solution, provide information on the strength of adsorption between sediment and humate, and provide information on the maximum amount of humate that can be adsorbed by the sediment. To determine the correct model that represents the adsorption behavior, the data is linearized and the straight line that best fits the data points is the one used to explain the sorption behavior by calculating the respective correlation coefficients (R^2). The Langmuir model assumes monolayer adsorption where adsorption can only occur at a finite number of definite localized sites that are identical and equivalent with no lateral interaction and steric hindrance between the adsorbed molecules. The graph is characterized by a plateau where once saturation point is reached, no further adsorption can take place. The isotherm is represented by the linear equation

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}.$$

q_e = mass of the humate adsorbed per unit mass of soil (mg/kg)
C_e = equilibrium solution concentration of humate (mg/L)
q_{max} = maximum adsorption capacity
b = energy of adsorption

By plotting the specific adsorption (C_e/q_e) against the equilibrium concentration (C_e), the constants b and q_{max} can be calculated. The Freundlich model assumes unlimited sorption sites where there is multilayer adsorption with non-uniform distribution of adsorption heat and affinities over heterogeneous surfaces. This model tends to represent heterogeneous materials better than other models. The linear equation is

$$\log(q) = \log K_F + 1/n \log c_{eq}$$

q = mass of the humate adsorbed per unit mass of soil (mg/kg)
C_{eq} = equilibrium solution concentration of humate (mg/L)
K_f = adsorption capacity
n = adsorption intensity

The linear equation from the plot of Log q vs Log C_{eq} gives K_f and n values.

When the Langmuir and Freundlich models are compared in Figures 10, 11, 12, and 13 for the four types of sediment, it can be seen that the Langmuir model is the one that best represents the adsorption data for the B1, B2, and B3 sediments showing that humic molecules bind and form a monolayer on the surface of the sediments. In the case of B4, it does not fit well because saturation of the surface with humate was not reached.
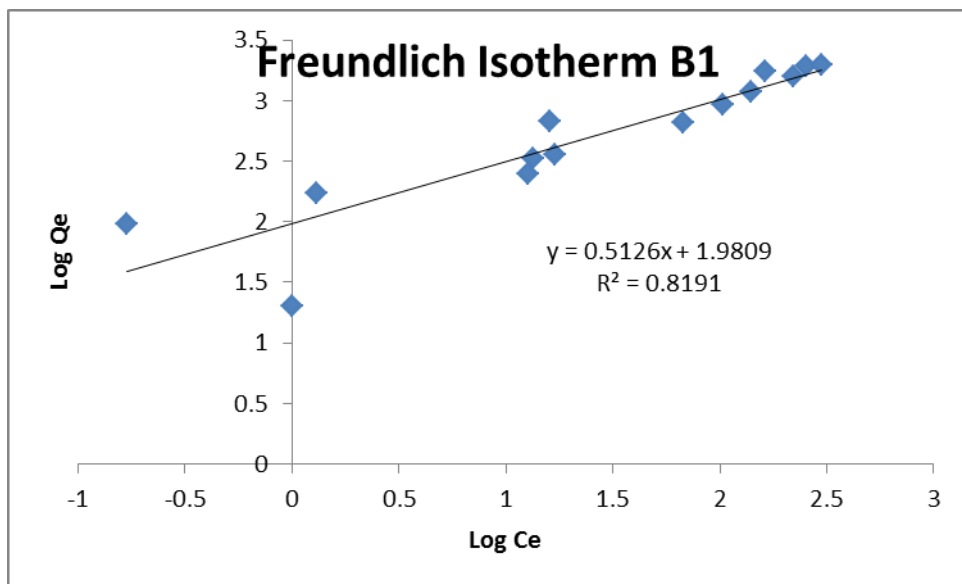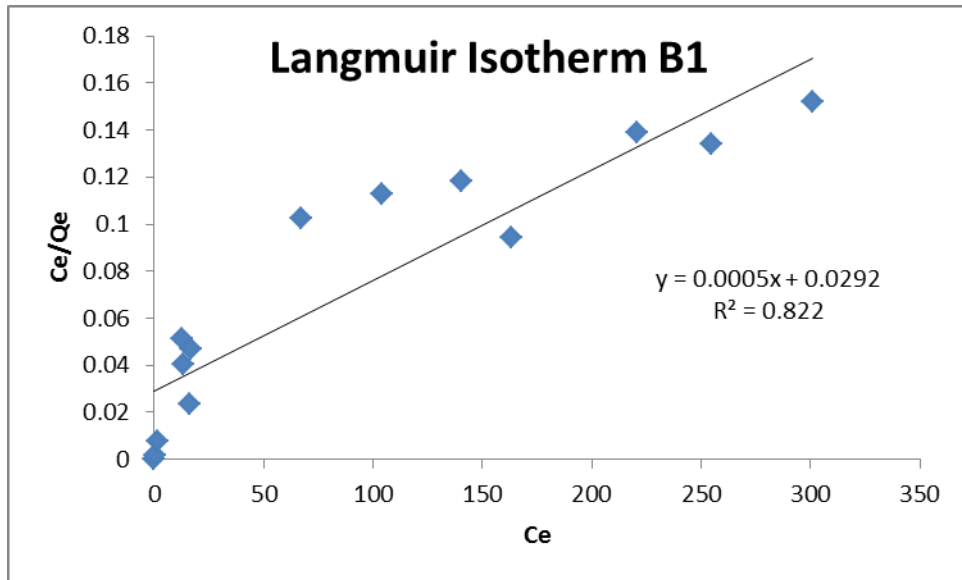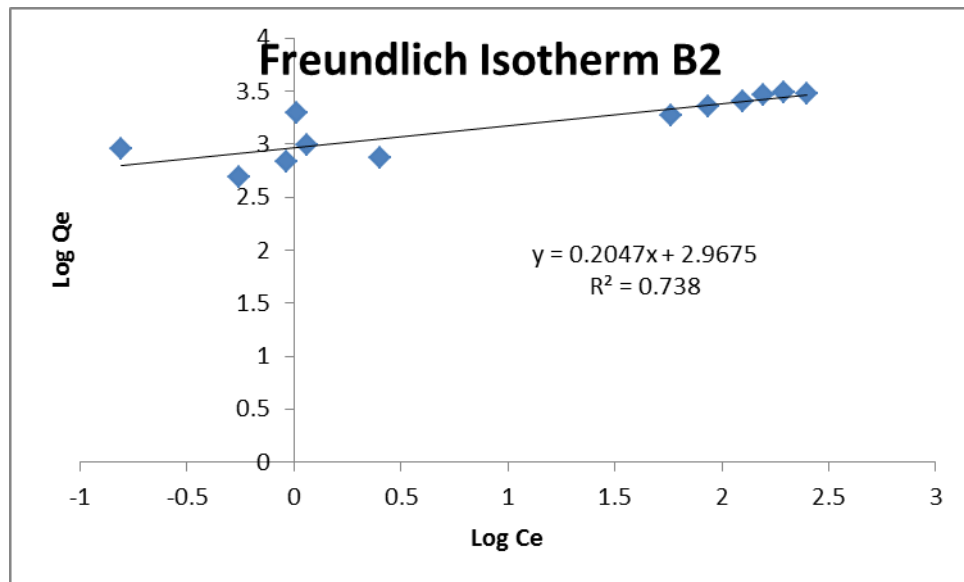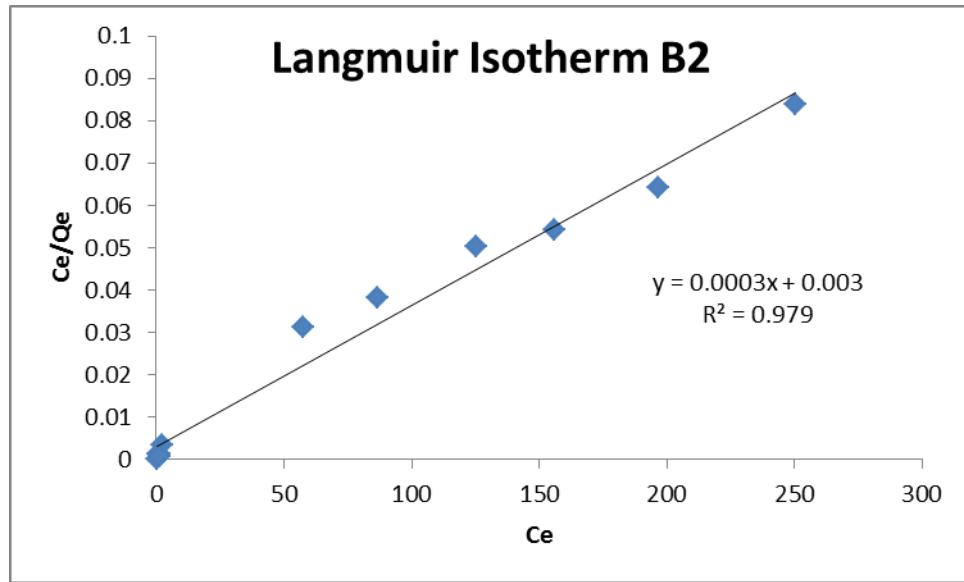
Figure 10. Langmuir and Freundlich isotherm B1.
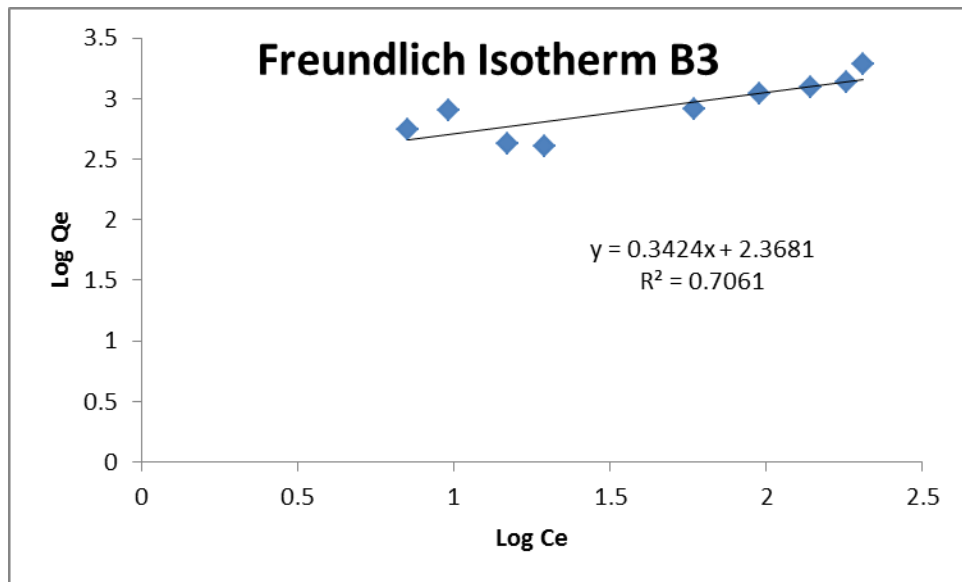
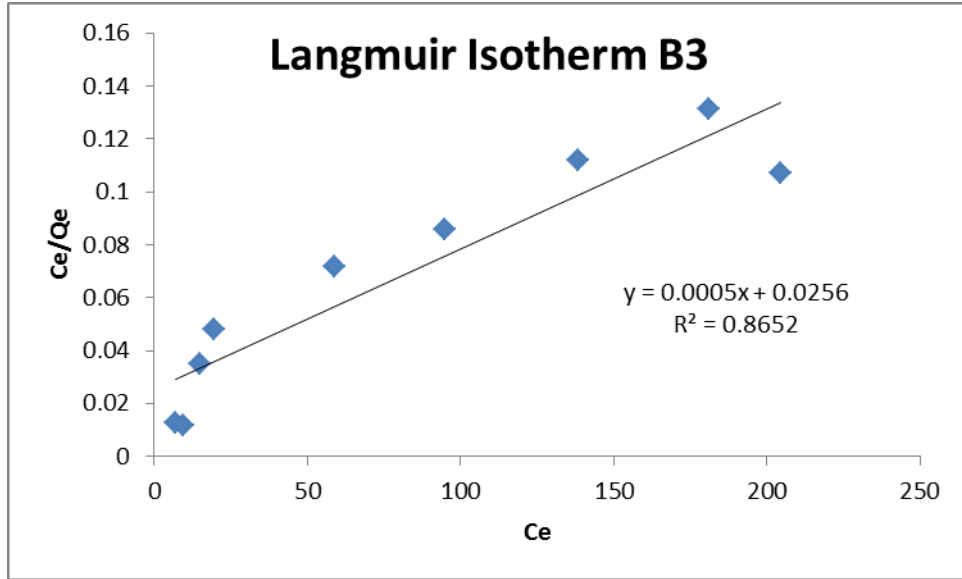**Figure 11. Langmuir and Freundlich isotherm B2.**

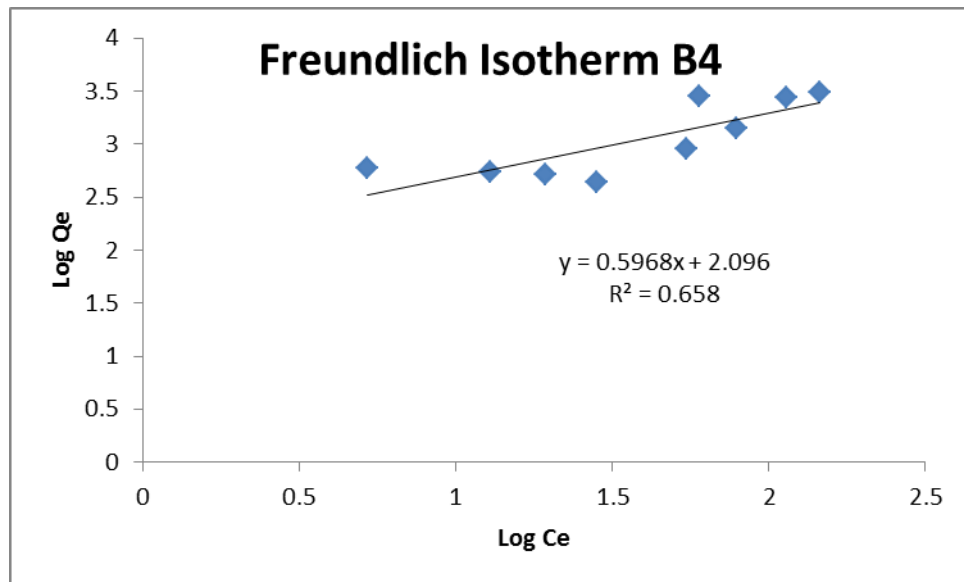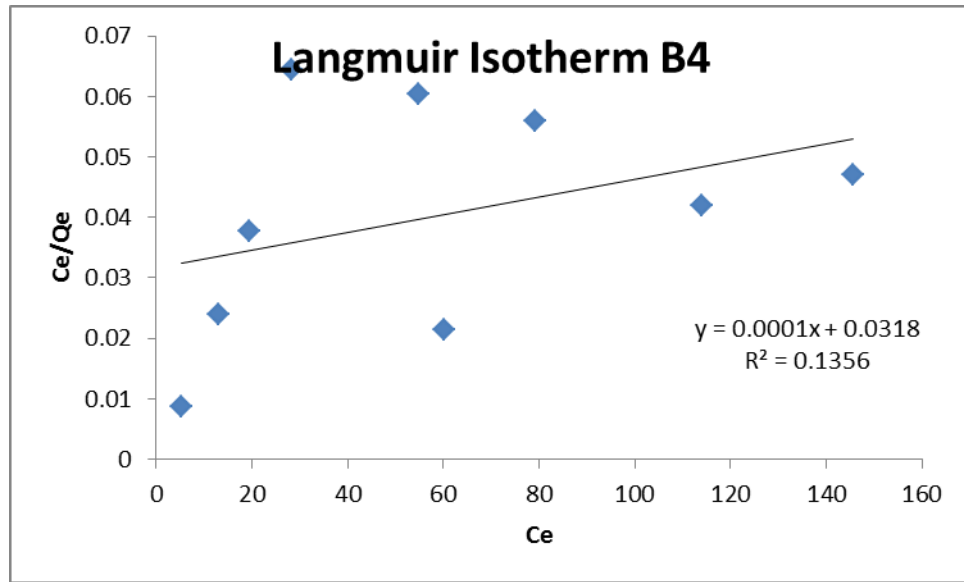**Figure 12. Langmuir and Freundlich isotherm B3.**

Figure 13. Langmuir and Freundlich isotherm B4.

From the equation of the straight line, Langmuir constants can be calculated: q_{max} which is the maximum adsorption capacity and b which is the energy of adsorption. The constant values are shown in Table 1.

Table 1. Langmuir Constants for the Four Types of Sediment

Type of sediment	q_{max}	b
B1	2000	0.017
B2	3333.3	1
B3	2.94	0.144
B4	1000	0.031

By comparing the four types of sediments, B4 seems to have a higher sorption capacity (q_{max} = 10000 mg/kg) than the rest of the sediments.

Desorption Experiment of Huma-K using four types of sediment at pH 4
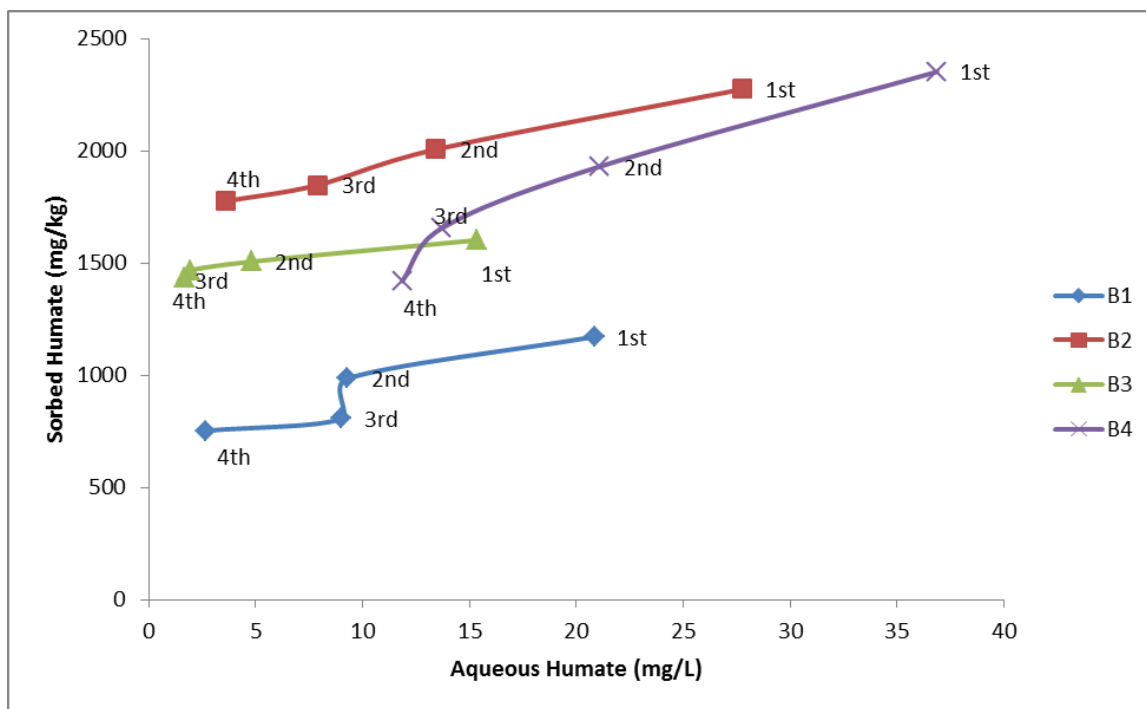
Figure 14. Desorption isotherm for the four types of sediment.

Figure 14 shows the desorption isotherm for the four types of sediments. The samples used in this desorption experiment were the 300 ppm samples for the four different types of sediment. In the 1st and 2nd desorption, the concentration of humate that is desorbed is higher than in the 3rd and 4th desorption. Probably the humic molecules that get desorbed in the first desorption are smaller and are interacting with other humic molecules through hydrophobic interactions. Another possibility is that smaller molecules occupy less sorption sites compared to bigger molecules, so the binding strength is weaker. In the 3rd

and 4th desorption, little humate is lost from the sediment especially for B1, B2, and B3. From the sequence of desorption experiments it can be concluded that humate will sorb to the sediments for a long time.

Determination of the E_4/E_6 ratio and the E_{ET}/E_{BZ} ratio

Since the humate solution prepared from Huma-K is an unrefined humate solution composed of humic acid and fulvic acid of different sizes and molecular weights, the E_4/E_6 ratio was used to determine which humic fraction is sorbed onto the sediments. The E_4/E_6 ratio is calculated by dividing the absorbance of the sample at 465 nm by 665 nm. Researchers have found that the E_4/E_6 ratio increases as the average molecular weight of humic substances decreases. The range of values of the E_4/E_6 ratio from a wide variety of sources for humic acids and fulvic acids are 3.8-5.8 and 7.6-11.5 respectively. In Table 2, the E_4/E_6 values for the four sequential desorptions are between 3-6, meaning that the fraction of humate bound to the sediments consists of humic acid molecules. As the third desorption is reached, the E_4/E_6 ratio is lower compared to the first desorption. From these results, it can be concluded that humic molecules of high molecular weight are more likely to resist desorption because they occupy more sorption sites, and humic molecules of low molecular weight will desorb first.

Table 2. E_4/E_6 Ratio

Sample Name	Sorption	First Desorption	Second Desorption	Third Desorption	Fourth Desorption
B1S1 300ppm	5.99	4.51	4.29	3.93	4.85
B1S2 300ppm	5.79	4.37	4.10	4.08	4.35
B1S3 300ppm	5.98	4.47	4.25	3.73	4.33
B2S1 300ppm	5.79	4.87	4.54	3.04	5.47
B2S2 300ppm	5.86	4.72	4.23	4.11	4.66
B2S3 300ppm	5.79	4.64	4.39	3.91	4.33
B3S1 300ppm	6.09	5.61	4.83	5.20	7.60
B3S2 300ppm	6.09	5.56	5.21	5.00	7.60
B3S3 300ppm	6.12	5.33	5.05	3.11	8.57
B4S1 300ppm	5.88	6.08	5.64	5.94	5.82
B4S2 300ppm	5.92	5.91	4.96	5.09	4.92
B4S3 300ppm	5.87	5.55	4.92	5.22	5.11

The E_{ET}/E_{BZ} ratio is calculated in order to determine the degree and possible nature of substitution. The ratio is calculated by measuring the absorbance at 253 nm and 220 nm corresponding to the electron-transfer band and the benzenoid band respectively. The intensity of the absorbance, especially the electron-transfer band, has a significant increase when substitution increases. The benzene band is almost unaffected. Low E_{ET}/E_{BZ} ratio indicates scarce substitution in the aromatic rings or substitution with aliphatic functional groups, and high E_{ET}/E_{BZ} ratio indicates presence of O-containing functional groups (hydroxyl, carbonyl, carboxyl, and ester groups) on the aromatic ring. The ratios vary from 0.03 (benzene ring), to between 0.25-0.35 for phenolic compounds and above 0.40 for aromatic rings with carbonyl and carboxylic groups.

The high values of E_{ET}/E_{BZ} ratios in Table 3 are indicative that the aromatic structures in these humic molecules probably have a higher degree of substitution with oxygen-containing functional groups.

Table 3. E_{ET}/E_{BZ} Ratio

Sample Name	Sorption	First Desorption	Second Desorption	Third Desorption	Fourth Desorption
B1S1 300ppm	1.04	0.87	0.88	0.90	0.93
B1S2 300ppm	1.02	0.88	0.89	0.92	0.94
B1S3 300ppm	1.03	0.88	0.88	0.91	0.96
B2S1 300ppm	1.01	0.85	0.86	0.89	0.88
B2S2 300ppm	1.01	0.86	0.87	0.89	0.90
B2S3 300ppm	0.99	0.86	0.87	0.88	0.88
B3S1 300ppm	1.04	0.93	0.87	0.96	0.88
B3S2 300ppm	1.03	-0.28	0.88	0.93	0.86
B3S3 300ppm	1.03	0.33	0.88	0.94	0.90
B4S1 300ppm	0.86	0.83	0.83	0.84	0.84
B4S2 300ppm	1.00	0.84	0.84	0.83	0.85
B4S3 300ppm	1.04	0.84	0.84	0.85	0.84

5. CONCLUSION

Form the experiments done during the internship, it can be concluded that different sediments have different sorption capacities for the Huma K, and these sorption capacities depend on the minerals present in the sediment and the number of sorption sites. Although in the desorption experiments some of the humic molecules sorbed to the sediment is desorbed, this desorbed fraction may be the fraction that was sorbed to the sediments through hydrophobic interaction with other humic molecules. Apparently, the humic molecules that remain sorbed to the sediments are not going to be desorbed because they have stronger binding interactions, so not all the humic molecules will desorb. The E_4/E_6 ratio from the sequential desorption of the 300ppm samples suggest that humic molecules of higher molecular weight are going to be sorbed first to the sediments because the ratio was lower in the third desorption than the other two desorptions. E_{ET}/E_{BZ} ratios showed that the humic molecules have a high degree of substitution in the aromatic rings. There is still much work to do in order to better understand the sorption and desorption behavior of this low cost humate solution on sediments, and also determine if it is possible to remove contaminants such as uranium using this humate solution.

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