STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

1-D COLUMN FLOW-THROUGH STUDY

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Development Initiative, an innovative program developed by the U.S. Department of Energy's Office of Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the spring of 2022, a DOE Fellow intern, Angel Almaguer, spent 8 weeks doing a summer internship at Pacific Northwest National Laboratory under the supervision and guidance of Dr. Jim Szecsody, Dr. Hilary Emerson, and Dr. Nikolla Qafoku of the Environmental Subsurface Science Group. The intern's project was initiated on June 27th, 2022, and continued through August 20th, 2022 with the objectives of elucidating the principles and mechanisms of contaminant transport in subsurface environments, as well as receiving guidance from PNNL mentors in the drafting of an experimental manuscript for Subtask 1.2.

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1. INTRODUCTION

Hexavalent chromium [Cr(VI)] contaminant plumes in Hanford's deep vadose zone (DVZ-1), perched water, and groundwater layers, located in the 200 Area pose a risk to human and environmental health. Chromium contamination originated from a variety of sources, however, primary mode of chromium (Cr) release into the environment has been through surface or near-surface spills and leaking tanks which used Cr-containing water as a corrosion inhibitor in nuclear reactors. When chromium is released into the soil and groundwater, it is present as one or more Cr^{VI} and/or Cr^{III} species. The most abundant aqueous species of Cr^{VI} include chromate (CrO_4^{2-}), $HCrO_4^-$ (<0.1 mol/L), and $HCr_2O_7^-$ (>0.1 mol/L); all of which are toxic to human health. Hanford's groundwater environment is slightly alkaline (pH 7.7 to 8.3) and oxic, which means Cr^{VI} as CrO_4^{2-} is expected to move rapidly through the vadose zone and groundwater layers with minimal sorption or geochemical reduction (Ginder-Vogel et al., 2005). The sorption of Cr^{VI} to soil is nearly non-existent at neutral and alkaline pH in aquifers, however, a considerable amount of CrO_4^{2-} sorption has been observed in acidic conditions (Zachara et al., 1989; Qafoku et al., 2009). Chromate mainly tends to sorb to Mn, Al, and Fe oxides, and clay minerals in Hanford's Ringold Formation sediment. Qafoku and Zachara have reported that aluminosilicate precipitate phases which form as alkaline water becomes neutral has previously been shown to coat and decrease the release rate of Cr into solution. Contaminated groundwater and soil remediation requires understanding the mechanisms involved in contaminant movement in the subsurface environment, to characterize the risks associated with it, as well as to develop emergency or remedial action plans. The partition or (distribution) coefficient (Kd) is the ratio of the contaminant concentration associated with the sediment to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium. It is used to estimate the potential for the adsorption of dissolved contaminants that are in contact with the sediment. Proper choosing of experimental parameters for 1-D column flow study, such as, sediment fraction, column dimensions, simulant solution flow rate, stop-flow events and dump durations, is necessary determining the contaminant retardation factor (Rf). The contaminant retardation factor (Rf) is a parameter used in transport models to describe the interaction between a contaminant and sediment, including surface adsorption, absorption into sediment structure, precipitation, and physical filtration colloids. Specifically, a Rf describes the rate of contaminant transport relative to that of groundwater. Once determined, an Rf can be used to calculate a Kd, or vice-versa.

In a 1-D column flow-through study, liquid that is spiked with a contaminant(s) is pumped through a soil column, and is designed to combine the chemical The benefit of flow-through column experiments is that they give a more realistic simulation of field conditions. In the field and in the lab, dissolution and precipitation and adsorption/desorption are the most important processes that influence a contaminant's interaction with the soil. The column experiment combines the chemical effects of sorption and the hydrologic effects of groundwater flow through a porous medium to provide an estimate of retarded movement of the contaminant of interest.

2. RESEARCH DESCRIPTION

A single 1-D Flow-through column experiment was conducted in SGW with hexavalent chromate (CrO_4^{2-}), a bromide (Br^-) tracer, and ≤ 2 mm Hanford formation sediment fraction. Effluent samples collected before and after designated stop-flow events were analyzed with UV-Vis spectroscopy to measure Cr^{VI} concentrations by calculating concentration data from absorbance data, and a bromide electrode to measure Br^- concentrations. The SGW solution matrix contained 200 µg/L of CrO42- and 80 mg/L (Table 4). Samples were collected with an HPLC pump with a flow rate of 0.48 mL/min (Hitachi L6000 series 0.001 to 10 mL/min. Br- tracer was used to evaluate the hydrodynamic dispersion and potential physical breakthrough tailing based on the breakthrough pattern of Br−.

Retardation factor calculations

$$\mathbf{R_f = v_p/v_c} \quad (1)$$

where,
v_p = velocity of the water through a control volume
v_c = velocity of contaminant through a control volume.

$$\mathbf{R_f = 1 + (p_b/n_e)K_d} \quad (2)$$

where,
$\mathbf{p_b}$ = porous media bulk density (mass/length^3)
$\mathbf{n_e}$ = effective porosity of the media at saturation.

Partition coefficient calculation

$$\mathbf{K_d} = \textit{Mass of Adsorbate Sorbed/Mass of Adsorbate in Solution}_i \quad (3)$$

$$\mathbf{R_f = 1+ bulk\ density*Kd/porosity} \quad (4)$$

$$\mathbf{K_d = (Rf-1)*porosity/bulk\ density} \quad (5)$$

Table 1: ***Column Dimensions***

Length (cm)	30.48
Diameter (cm)	2.36
Column Area (cm^2)	4.374
Column Volume (cm^3)	133.33
Pore Volume (cm^3)	~47, < 1000 psi

Table 2: ***Column, sediment, moisture, and porosity measurements***

Empty Column Weight (g)	669.72
Packed (unsaturated) Column Weight (g)	911.07
Packed (saturated) Column Weight (g)	949.28
Sediment Weight (g)	242.47
Water Weight (g)	37.58
Moisture Content (g/g)	0.15
Porosity	0.2807
Total Pore Volume (mL)	38.14
Bulk Density (g/mL)	1.819

Table 3: ***SGW Formulation***

Chemical	Concentration (µg/L)
H_4SiO_4 Silicic Acid	110
KCl, Potassium chloride	120
$MgCO_3$, Magnesium Carbonate	110
NaCl, Sodium Chloride	150
$CaSO_4$ Calcium Sulfate	170
$CaCO_3$, Calcium Carbonate	190

3. RESULTS AND ANALYSIS

The R_f value obtained for the adsorption portion of the Cr^{VI} breakthrough curve was 1.126, at 4.393 pore volumes. The K_d value for the adsorption breakthrough curve was calculated using the retardation factor for the same portion of the breakthrough curve, and was calculated to be 0.020 mL/ using equations (**1**, **2**, and **3**).

The R_f value obtained for the desorption portion of the breakthrough curve was found to be 0.891 and the K_d value calculated from was 0.15 mL/g , for the desorption end of the breakthrough curves using equations (**1**, **2**, and **3**). The total mass loss of Cr^{VI} by the end of the column experiment was calculated to be 0.865 g. Retardation factors (R_f) at the adsorption and desorption limbs of the breakthrough curve were calculated by taking the difference of the first sample's pore volume (PV) after the end of the first stop-flow event, and the cumulative $PV*C/C_0$ value from the last sample of the stop-flow event. For the desorption limb of the Cr^{VI} breakthrough curve, the R_f was calculated by taking the difference between the cumulative pore volume (cum. $PV*C/C_0$) value from the sample at the end of the last dump event and the (cum. $PV*C/C_0$) value from the last sample of the first dump event.

Table 4: ***Pore volume per hour (hr) and hr per pore volume***

Pore Volume (mL)	
hr/PV	0.7073
PV/hr	1.4138

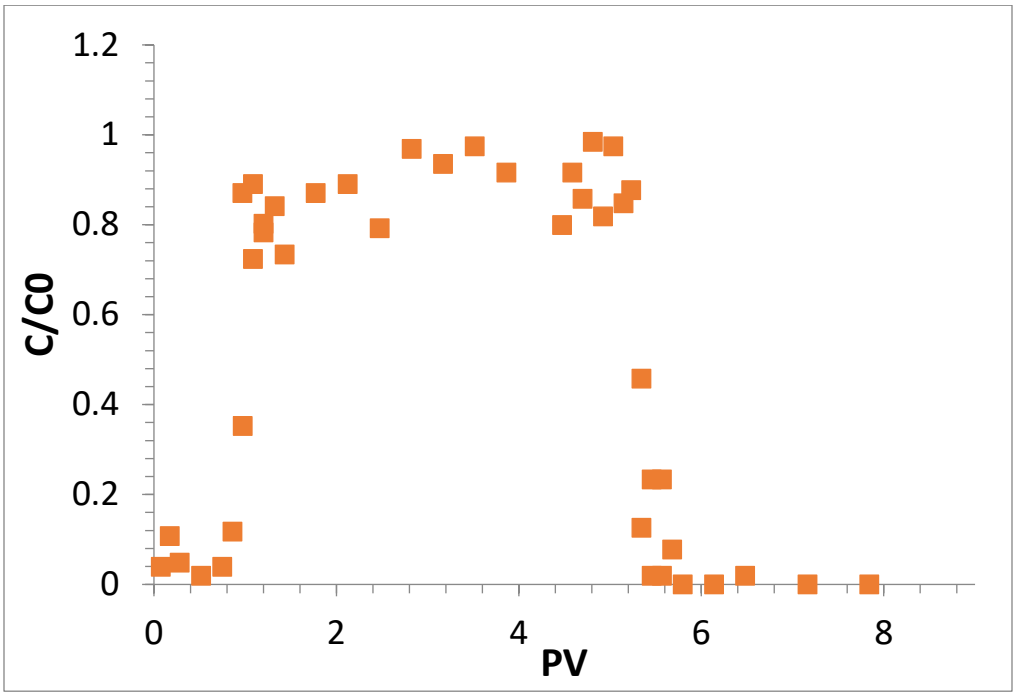

Figure 1: ***Cr^{VI} breakthrough curve***

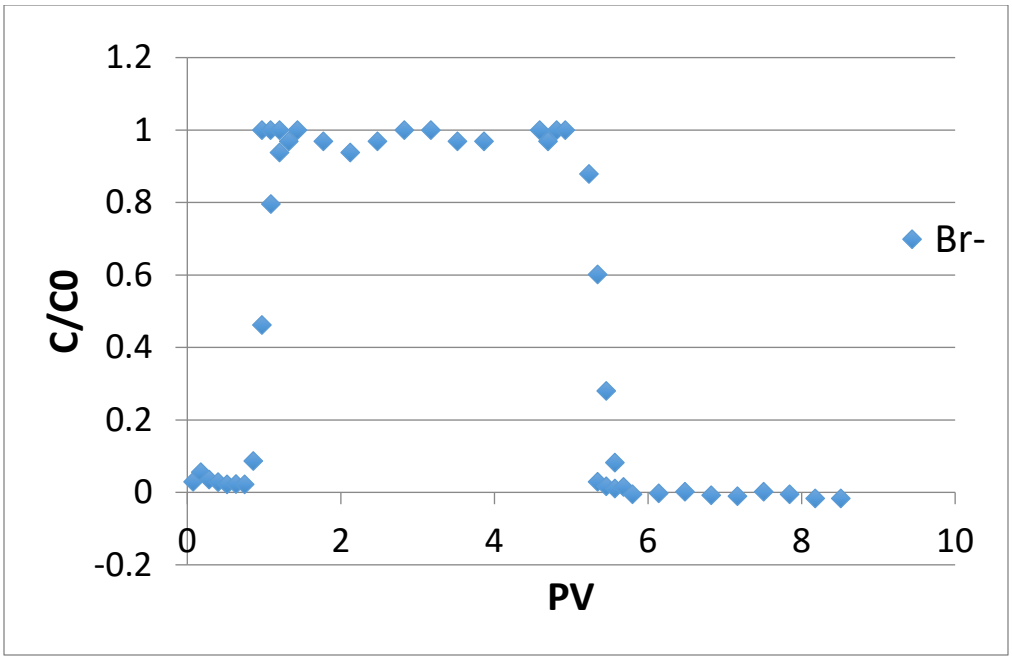

Figure 2: ***Br⁻ tracer breakthrough curve***

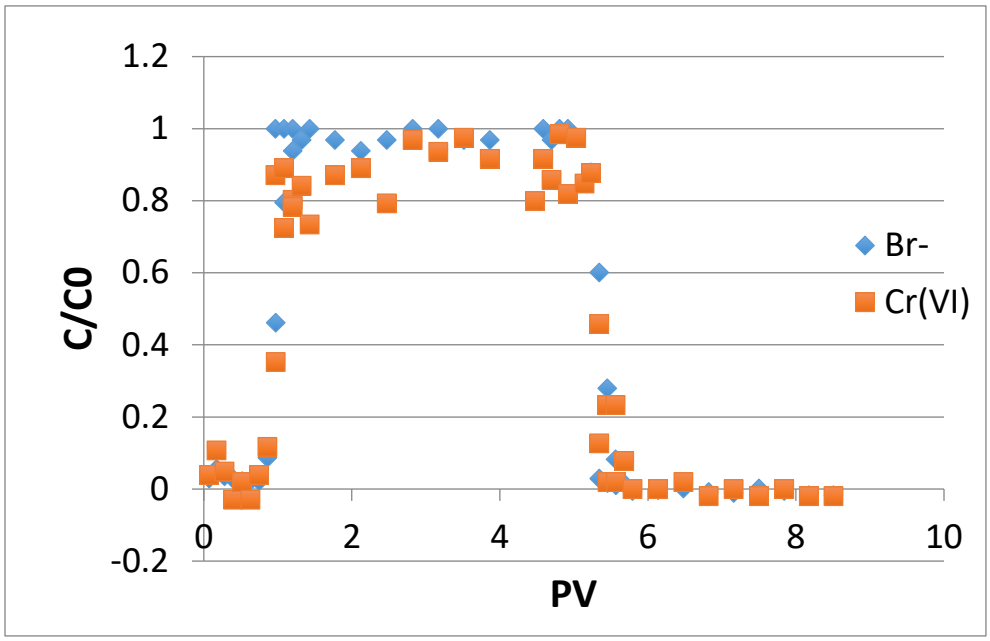

Figure 3: ***Normalized Cr^{VI} and Br^- breakthrough curves***

4. CONCLUSION

In conclusion, the results of the experiment showed that Cr^{VI} tends to undergo fairly predictable sorption and desorption processes in neutral to alkaline groundwater, when in the presence of Hanford formation sediment. Some mass loss of Cr^{VI} could be attributed to the natural presence of Mn, Al, and Fe oxides, and clay minerals in the Hanford sediment. It has also been observed that the choice of sediment particle fraction size greatly influences the resulting R_f and K_d values calculated at the adsorption and desorption limbs of the breakthrough curves produced. The concentrations of contaminant and trace are used were analyzed via UV vis spectroscopy and he bromide probe, respectively. It has been noted that for a more accurate measurement of concentration, ICP-MS and ion chromatography (IC) should be used for future analyses.

5. REFERENCES

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