Sorption and Elution of Slow Release Electron Donor to Support Biological Reduction of Chlorate and Perchlorate

Group 1

Yasaman Saedi (saediy1@unlv.Nevada.edu), **Sichu Shrestha** (sichu.shrestha@unlv.edu), **Jacimaria Batista** (jaci.batista@unlv.edu) (University of Nevada Las Vegas, NV, USA), **Nicole Martin** (martin40@unlv.nevada,.edu), **John Michael Gonzales**(gonza982@unlv.nevada,.edu)

Ronnie Britto (Ronnie.Britto@tetratech.com)(Tetra-Tech, Collierville, TN, USA)

Background and Objectives

Perchlorate (ClO_4^-), a strong oxidizer in explosives production, is an inorganic contaminant which has been detected in groundwater and soil systems throughout the US and other countries for last two decades. Since, perchlorate interferes with the thyroid gland function and inhibits iodide uptake in humans and animals, perchlorate removal from surface and groundwater is a vital need. Although, there are no federal drinking water standard for perchlorate yet, several states including California and Massachusetts have established drinking water standard level varying from 1 to 18 micrograms per liter (µg/L) for this contaminant. A significant feature of perchlorate is its high solubility and stability in the aqueous phase. Fortunately, in the environment, naturally occurring bacteria in groundwater and soils are able to reduce perchlorate to innocuous chloride. In most contaminated sites, nitrate and chlorate are co-contaminants along with perchlorate.

Among existing technologies for perchlorate removal, biological reduction is a promising treatment approach. Perchlorate (ClO_4^-), as an electron acceptor, can be reduced to chlorate (ClO^-_3) and then to chloride (Cl^-) by perchlorate-reducing bacteria (PRB) under anaerobic conditions and in the presence of an electron donor. It has been noted that all PRB are able to reduce chlorate, whereas some of them can also remove nitrate. Biological reduction of perchlorate and co-contaminants requires the addition of an electron donor/carbon source. Emulsified vegetable oil substrates (EOS) have been successfully used to remediate perchlorate in the US. EOS-PRO which has been applied for this research is a specific type of EOS that contains nutrients and small droplet size. **The main objective of this research is to evaluate the biodegradation potential of nitrate, chlorate, and perchlorate using EOS-PRO as electron donor in actual contaminated soils and groundwater.** Because biological perchlorate reduction can take place in situ, **another goal of this research is to understand how EOS-Pro sorbs and elutes from actual saturated soils that hold contaminated groundwater.** Such understanding can guide application frequency of EOS –PRO for in-situ bioremediation of sites contaminated with perchlorate.

Experimental Approach

In the microcosm tests, two different soil types were used. The amounts of oil added to each microcosm were 0.02 g of oil/ g of soil and 0.01 g of oil/ g of soil for QAL and UMCF, respectively. Research approach for the microcosm tests addressed the potential biodegradation of chlorate and perchlorate in actual contaminated soils and groundwater using EOS-PRO with no bio-augmentation. In the column studies, two UMCF and QAL soils were packed in the columns to mimic different groundwater velocities. For fine sediments the columns were pressurized at 5-10 psi, using an in-house built pressure valve. For the oil sorption batch test, varying amount of soils with a certain amount of EOS-PRO solution were thoroughly mixed in a rotatory shaker for 24 hours.

Table 1: Perchlorate and Chlorate Concentrations in Soils and Groundwater

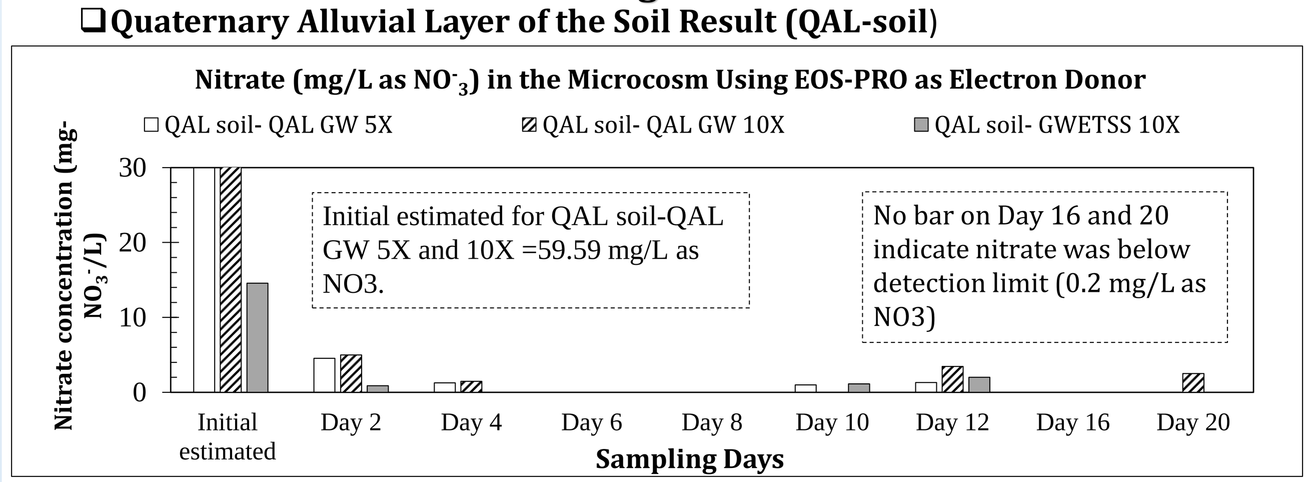
Sample ID	Chlorate Concentration in Soil (mg/kg)	Chlorate Concentration in Groundwater (mg/L)	Perchlorate Concentration in Soil (mg/kg)	Perchlorate Concentration in Groundwater (mg/L)
UMCF	< 0.01	9.86	< 0.01	6.66
QAL	3.882	51.40	1.252	12.50

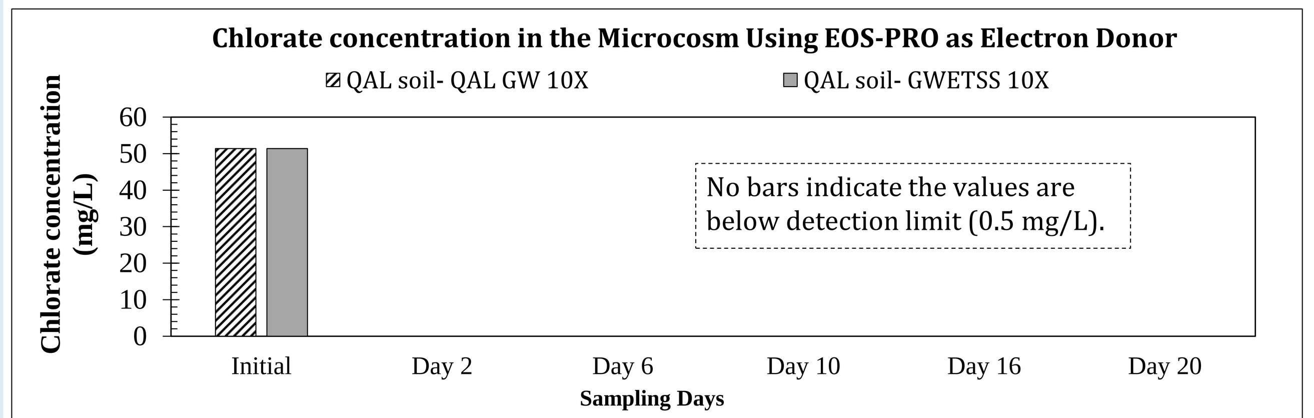
Microcosms

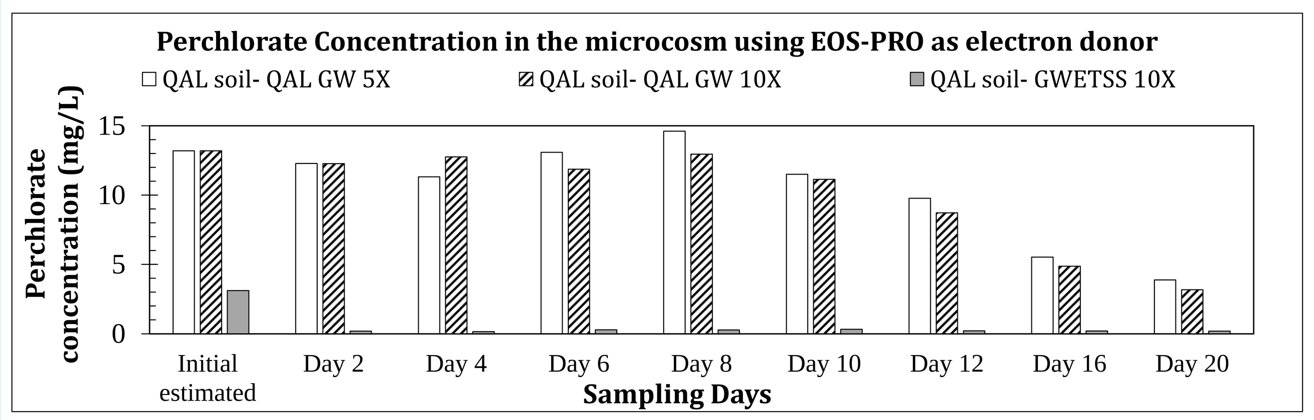
Microcosm tests were performed using two types of soils and three types of groundwater from an actual contaminated site. Soils were collected from two different horizons, Quaternary Alluvial layer (QAL) and Upper Muddy Creek Formation (UMCF) layer. EOS-PRO was used as electron donor to support bioremediation of chlorate and perchlorate. Thirty grams of each soil were added to 125 mL autoclaved borosilicated glass bottles. One hundred mL of the desired groundwater was transferred along with EOS to the glass bottles containing soils. No nutrient was added to the bottles because EOS-PRO contains vitamin B12 and phosphate. The glass bottles were crimpled closed using an aluminum seal and a butyl rubber septum and were placed in a rotary shaker at 30 rpm and 22 °C. At pre-determined time intervals, the glass bottles were sacrificed in order to determine the concentration of perchlorate, chlorate, and nitrate remaining.

Results of Batch Microcosms Using EOS-PRO

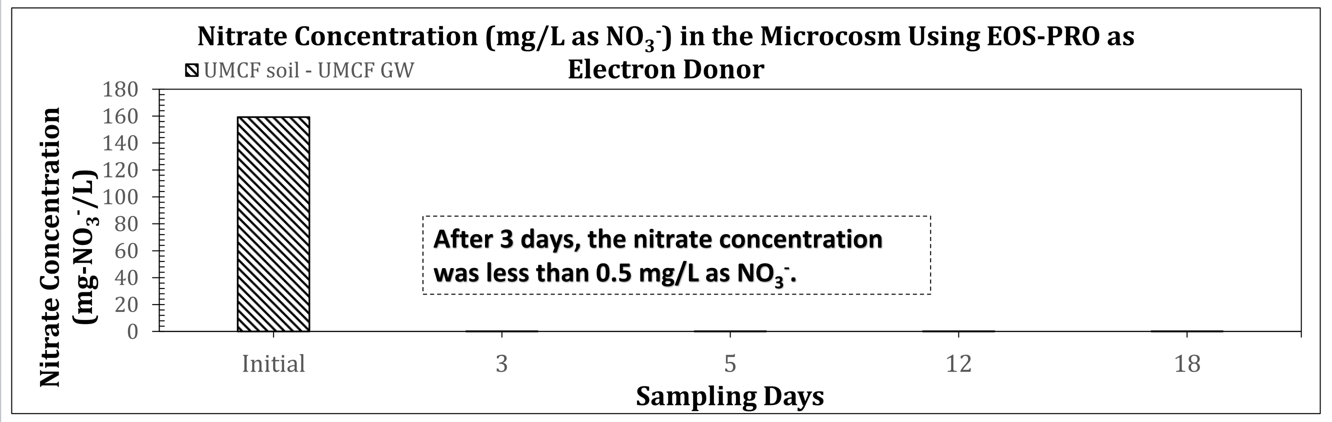
❑Quaternary Alluvial Layer of the Soil Result (QAL-soil)

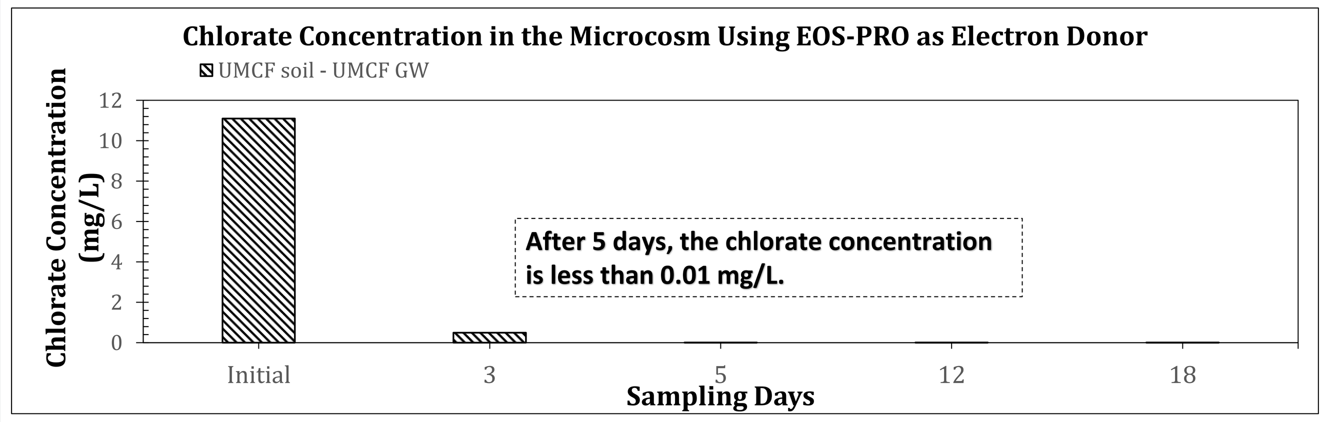


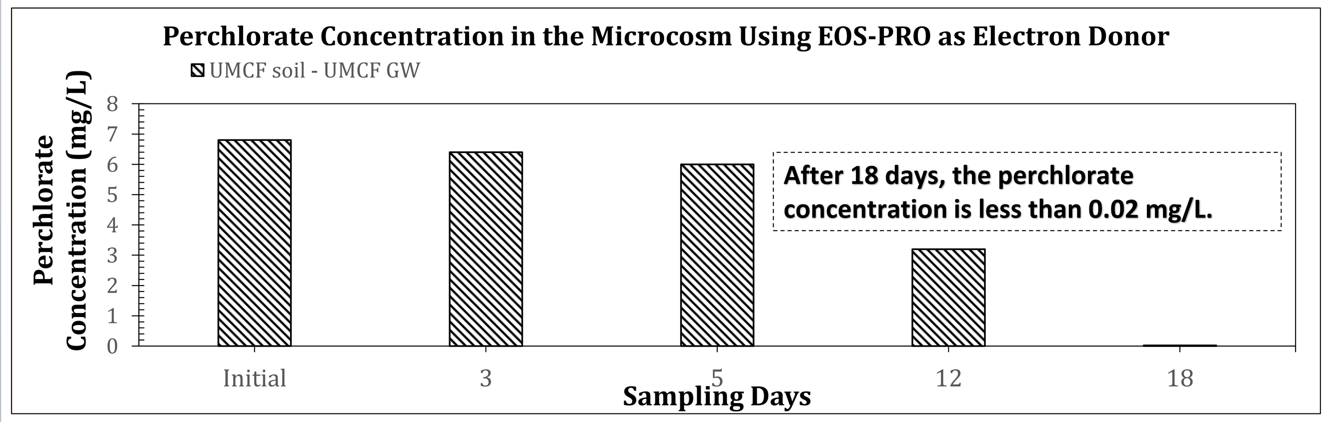




❑UMCF Layer of the Soil Result







Oil Sorption Batch and Column Tests

Oil sorption batch sorption tests were performed in three soil types, QAL, UMCF, and UMCF-LV. In the tests, various amounts of soils (5, 10, 20, 25, and 30 g) were added to prepared EOS-PRO solution, containing 20 g of oil per 100 ml of deionized water. After 24 hours of mixing the samples in a rotatory shaker, the contents of the bottles were poured into aluminum dishes and placed in an oven for 24 hours to remove excess water. Aluminum dishes were then transferred to a furnace at 550 °C in order to ignite the oil. The mass of oil sorbed per gram of soil was computed by subtracting the weight of soil residual after ignition from the weight of soil before ignition.

For the oil elution test, clear PVC columns were packed with dried soil (105 °F) to simulate groundwater velocity and permeability. Eight columns were built for oil adsorption testing for two different oil concentrations (low and medium) and two soil types (UMCF and QAL). All QAL columns were pressurized at 5 psi, whereas UMCF columns were running at 10 psi. For the low oil saturation test, a diluted EOS-PRO solution (1 part of EOS-PRO diluted in four parts of QAL or UMCF groundwater, 1:4), at about 13% of the maximum oil saturation capacity, was injected into the saturated columns. The COD of the diluted EOS-PRO was 400,000 mg/L. Furthermore, for a medium oil saturation test, EOS-PRO (1 part of EOS-PRO diluted in three parts of QAL or UMCF groundwater, 1:3) at about 45% of the maximum oil saturation was injected to the water-saturated columns. The COD of the diluted EOS-PRO was 500,000 mg/L. The oil dilution ratio (1:3) was decreased as compared to that used in the low oil saturation test (1:4) because the goal was to inject more mass of EOS-PRO.

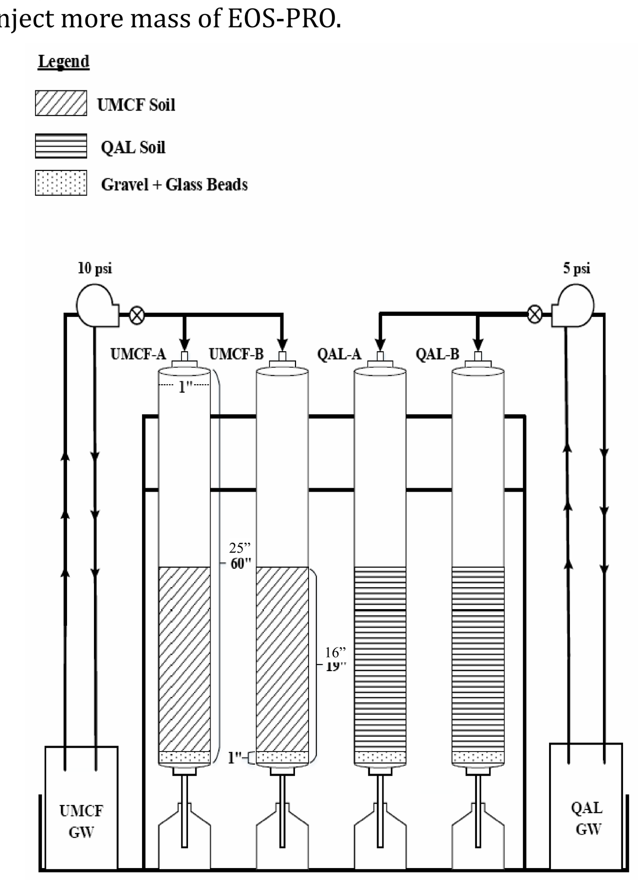
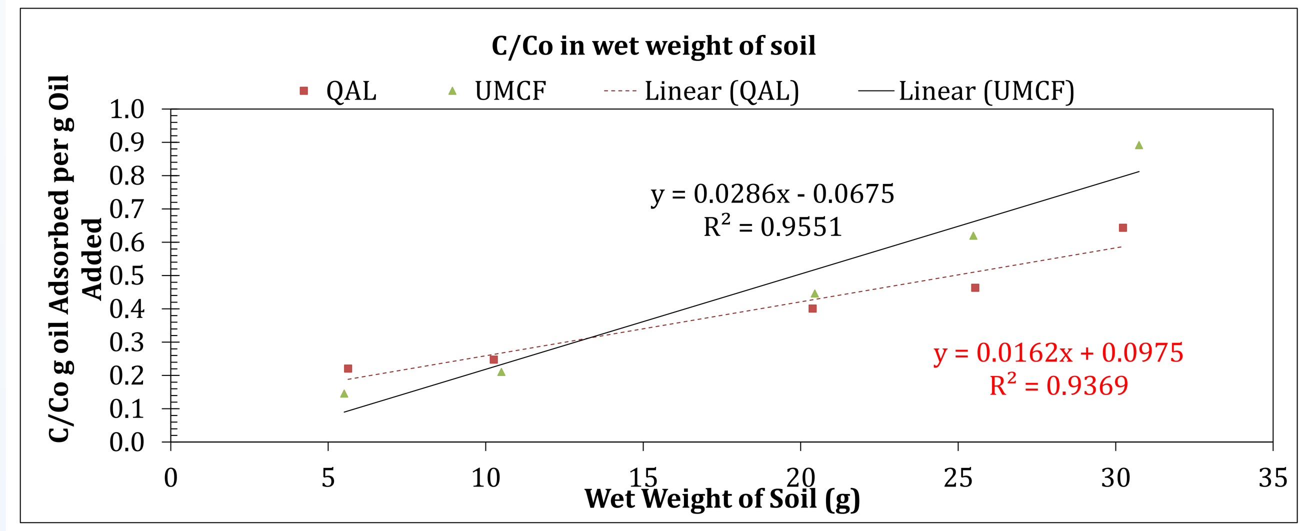
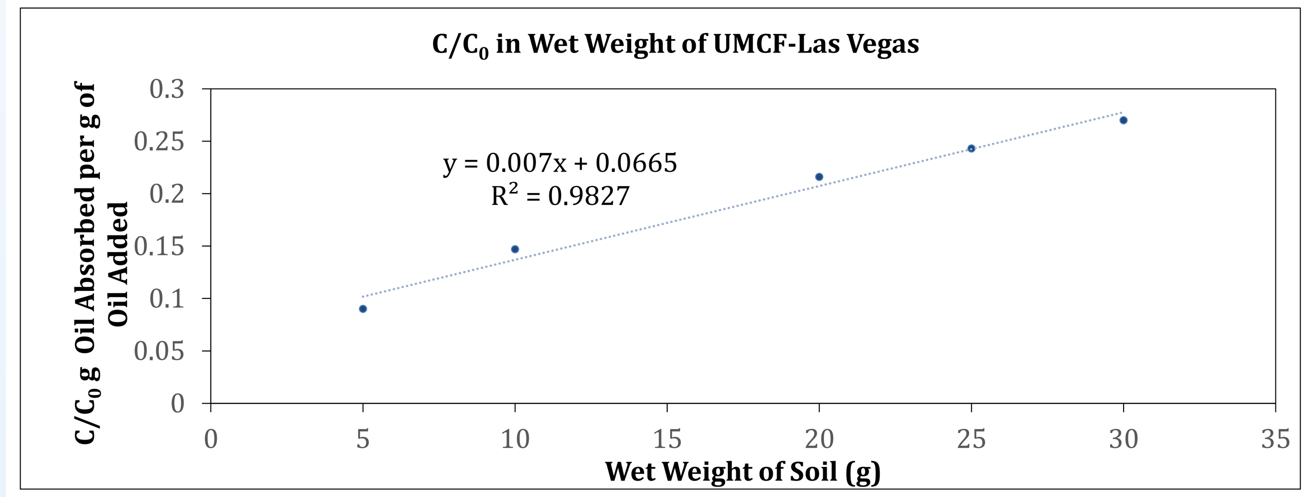


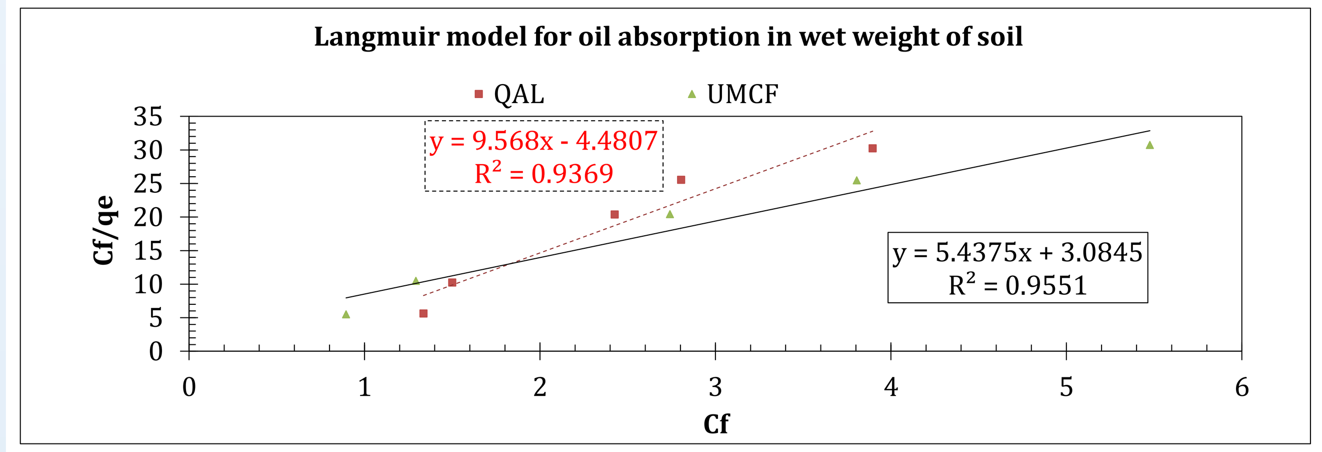
Figure 1: Schematic of Column Setup for EOS-PRO oil Elution Testing

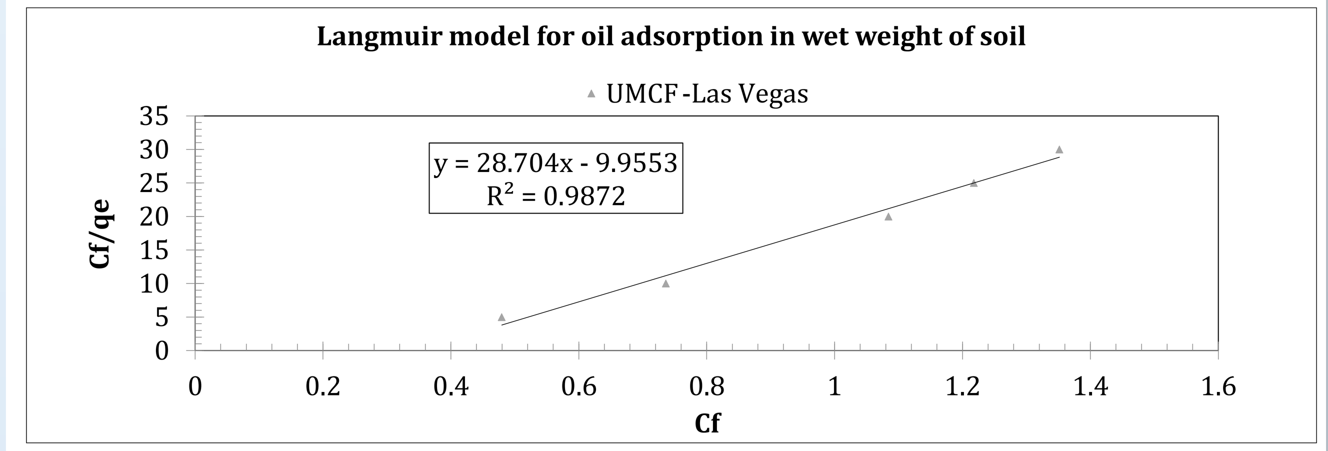
Results of Oil Sorption in Batch Test



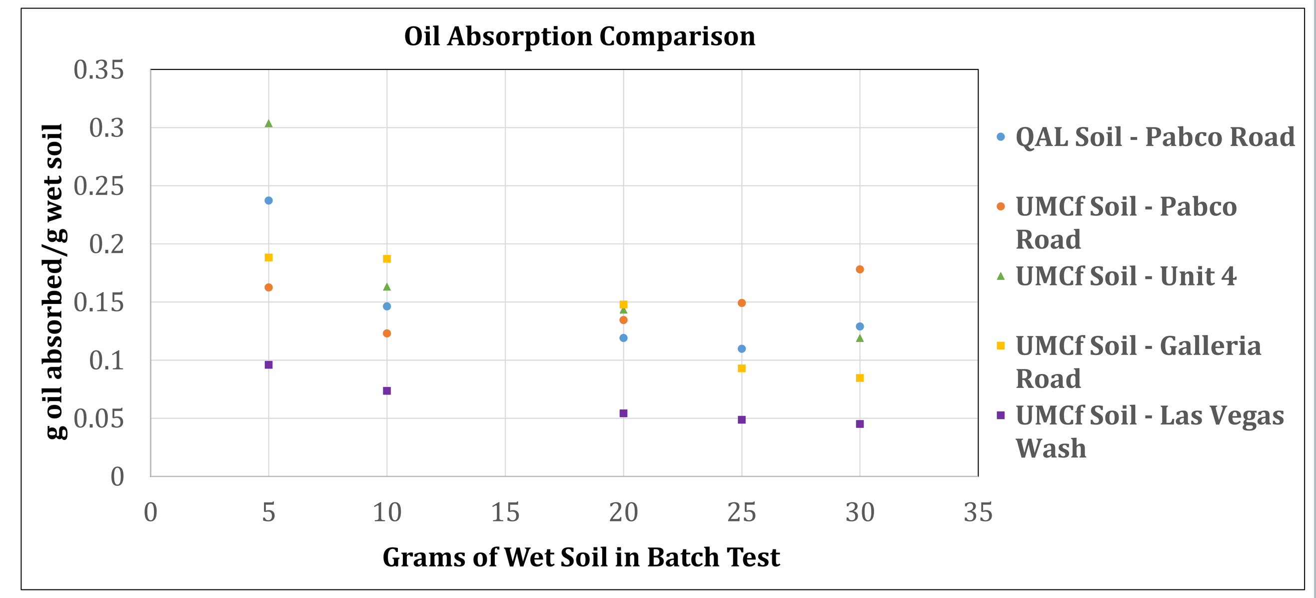


Langmuir Isotherm Results

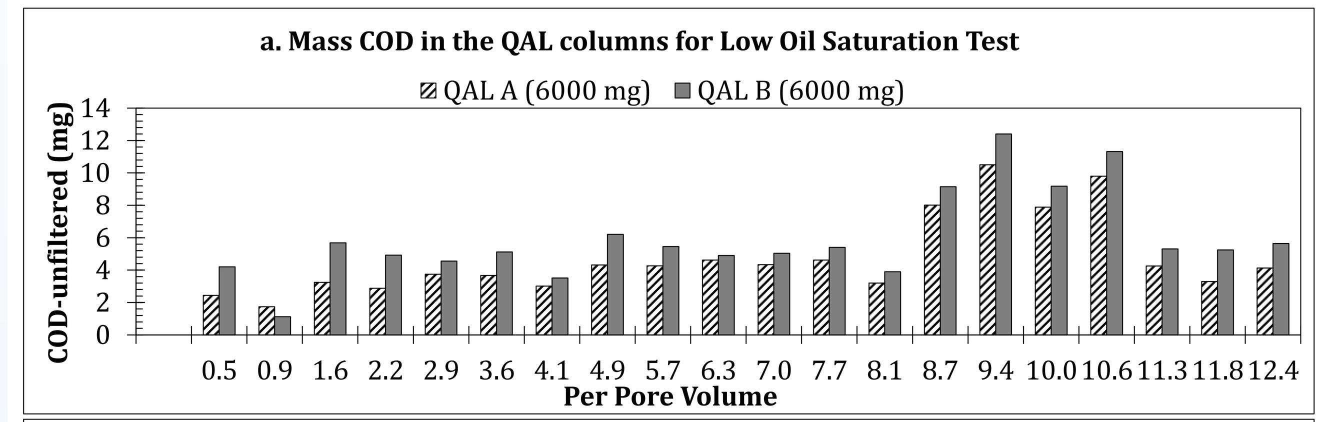


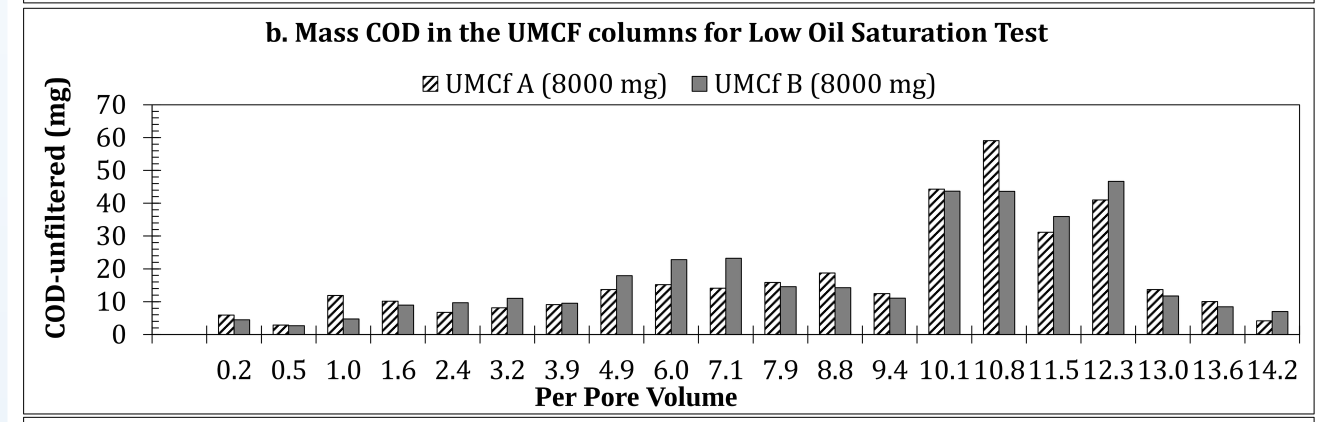


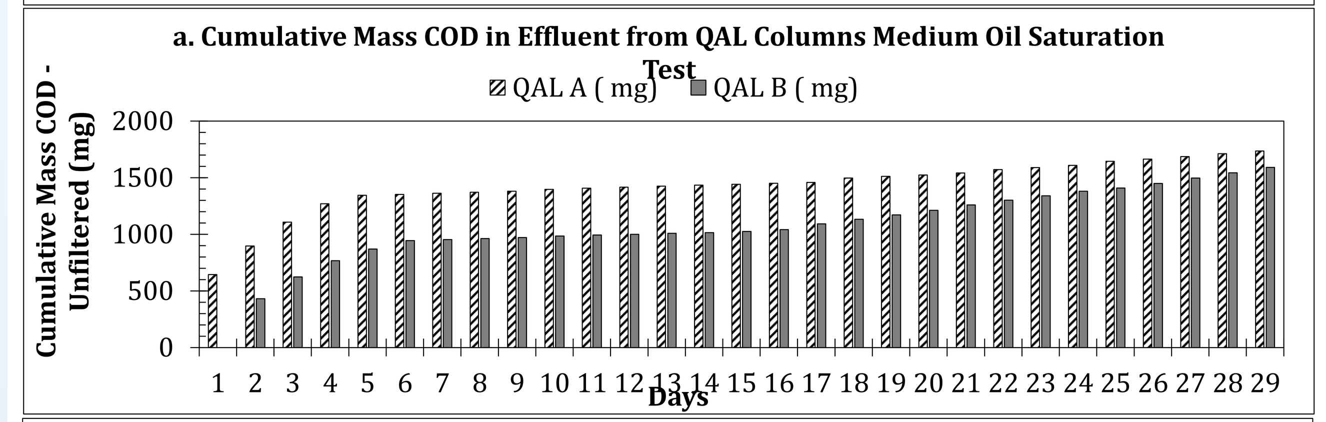
Oil Sorption Batch Test Comparison for different soils

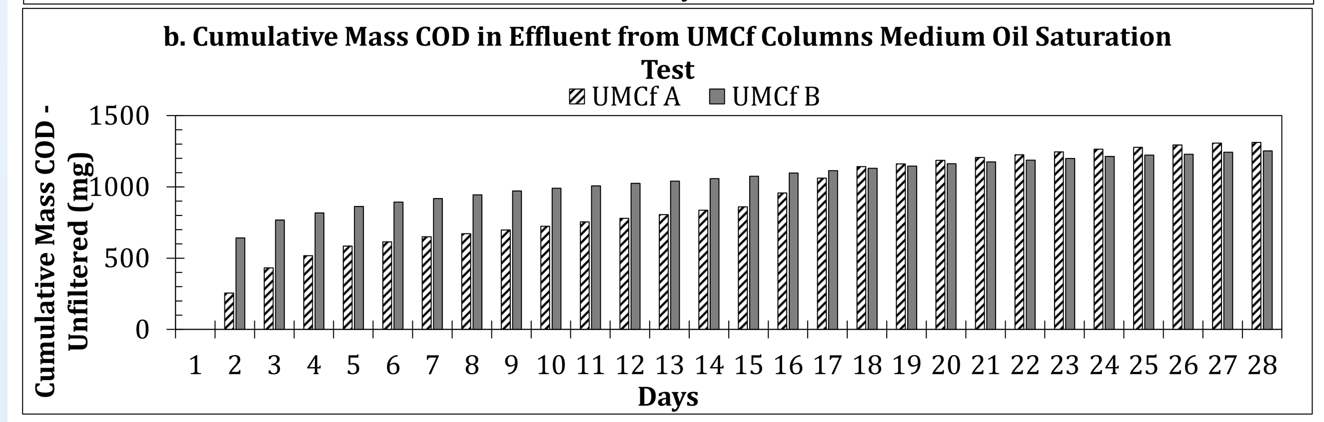


Results of Oil Desorption in Column Tests









Major Findings

- EOS-PRO was an effective carbon source to degrade nitrate, chlorate, and perchlorate under anaerobic conditions.
- The microcosm results indicated that since there was no significant difference in the kinetic rates between a 5X stoichiometric ratio of oil as compared to 10X, 5X oil addition is sufficient to promote the degradation of the all contaminants.
- The results show that 2x stoichiometric ratios of emulsified oil resulted in full degradation within 20 days in both QAL (alluvial soil) and UMCF (clayey soils). Even using 2x stoichiometric oil ratios resulted in oil remaining in solution after all contaminants were degraded. Therefore, the EOS-PRO dosage can be decreased.
- Initiation of perchlorate degradation was delayed by the presence of nitrate and chlorate. Perchlorate degradation occurred within 20 days of running the test for both horizons. Therefore the order of degradation is Nitrate> Chlorate> Perchlorate
- The sorption batch test results revealed that UMCF soils absorbed more oil than QAL for the same amount of the oil. In addition, the isotherm plots revealed that the oil sorption obeys Langmuir isotherm with coefficient of q_{max} = 0.1045 g oil/g for QAL wet soil, q_{max}= 0.184 g oil/g for UMCF wet soil, and q_{max} = 0.034 g oil/g for UMCF-Las Vegas wet soil.
- The amount of oil that is sorbed to soils is highly dependent on soil type. Clayey soils sorbed more oil than sandy ones. A soil containing montmorillonite clay sorbed much oil, but almost done was eluted. Therefore, it is important to investigate sorption and elution of oil from the soil on which bioremediation will be performed. While higher sorption is desirable to minimize rea-application frequency, stronger sorption is undesirable as the oil would not be released to the groundwater for bacteria use.
- Based on the oil sorption and desorption results, it can be concluded that saturating QAL and UMCF soils to 13% and 45% of their capacity produces eluates containing 100-200 mg COD/L and 600-1000 mg COD/L, respectively. Although higher amounts of oil adsorb to the soil when more oil is applied, the concentration of oil eluted is a function not only of the amount of oil applied, but also of the amount of water that is flushed through the system.

Acknowledgements

We would like to thank Tetra-Tech for funding this research. We also would like to thank Mr. Brad Elkins from EOS Remediation, LLC for providing emulsified oil samples for this research.