Determining a bioventing scale-up factor

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Bioventing is an increasingly popular means of removing hazardous petroleum products from sites contaminated through industrial spills and leaking underground gasoline storage tanks. In order to design the appropriate bioventing system and estimate clean-up time, biodegradation rates are needed. Consequently, a mesoscale bioventing reactor system was used to determine the degradation rate of synthetic gasoline in two soils, Delhi sandy soil and Elora clayey soils. Additionally, the mesoscale rates were compared to rates from previously completed research using smaller scale reactors that held about 150 g of soil, to determine the scale-up factor. In total, ten 4 kg reactors were spiked with synthetic gasoline to an initial concentration of 4000 mg/kg soil. Vacuum was then applied to the mesoscale reactors at a rate of 0.75 mL/min, with sufficient water content to maintain bioventing conditions. Gas chromatography was used to determine concentrations of synthetic gasoline in the soil every two days. Results indicate a smaller scale up factor for Delhi, when compared to the Elora soil. Furthermore, it was observed that the mesoscale reactor had a slower decay rate than the small scale reactor, suggesting that the decay rate decreases with an increase in reactor size. As a result, conservative estimates are needed when transferring lab degradation data results to field scenarios.

Petroleum products are used worldwide and pose both environmental and health risks when not properly managed. Petroleum contamination is most common in areas used for industrial applications, and gasoline stations containing leaking underground storage tanks. A variety of ex-situ and in-situ remediation techniques have been developed such as vapour extraction, soil washing, and solvent extraction. However, these methods are costly. In addition, they leave behind varying amounts of petroleum products in the soil, meaning that the site has not been fully remediated [1].

Bioventing is an in-situ treatment method that is commonly classified as biostimulation. It works by encouraging natural occurring petroleum degrading microbes to use the petroleum contaminants as a carbon source through the addition of oxygen and nutrients. Nitrogen is the typical nutrient needed. Research was previously completed to determine the degradation rate in bench scale reactors containing 150 g of soil [2] and develop a universal degradation correlation. However, further work is required with larger reactors to see if scale-up factors are present [3], to make it easier to transfer the laboratory results to the field. Accordingly, two different soil types were tested in mesoscale reactors holding 4 kg of soil. The resulting degradation coefficients would allow comparison of

bioventing performance from the 150 g experiments and help evaluate the scale-up factor.

METHODOLOGY

Soil

Soil was collected from two agricultural research centers in Delhi and Elora, Ontario. These soils were distinct due to the sandy composition of the Delhi soil, and clayey composition of the Elora soil. Both soils were dried outside during warm weather and then sieved using a 2 mm screen to remove gravel. Seven days prior to use, and before the addition of hydrocarbon, 4 kg of soil was weighed and rehydrated with 500 mL of water, and then spiked with 5.45 g of ammonium chloride to allow the microorganisms to repopulate the soil [4].

Reactor Setup

Twelve individual reactors were set up using the two soil types (Elora and Delhi) each containing 4 kg of dry soil. Ten reactors were spiked with 32g of synthetic gasoline, while two reactors remained uncontaminated to monitor the soil moisture content. Reactors consisted of a perforated metal side that allowed radial air flow, while both top and bottom portions of the reactors were sealed to limit axial evaporation and short circuiting. Figure 1 shows a picture of

Figure 1. Picture of bioventing reactor and vacuum pumps.

a typical reactor along with the vacuum pumps providing the minimal airflow.

Monitoring and Maintaining Conditions

The desired soil moisture content was 50% of the field capacity value and this was monitored using a reflectometer in the unspiked reactors. Water was then injected into the reactors daily through three top mounted ports to maintain consistent water content of 6-12% (target 9%) for Delhi and 9-15% (target 14%) for Elora.

Constant airflow through the soil, which provided the required oxygen for the hydrocarbon degraders, was achieved through the use of Gilian Low Flow Pumps. A vacuum of (0.75) mL/min was applied to each reactor through a center mounted perforated steel column. Air flow through natural evaporation was minimized by having a sealed top and sealing sampling ports when not in use.

Sampling and Analysis

Samples were taken every two days through ports on the top of the reactors. A probe tool was used to get a soil sample reflecting the entire vertical profile of the reactor. From the sample taken, approximately 3.3 g of soil was placed in a vial containing 10 mL of methylene chloride (MeCl) solvent and 5.45 g of ammonium chloride (NH₄Cl). Samples were sealed and stored in a freezer until further analysis.

Prior to analysis, samples were shaken using a wrist shaker twice for 30 minutes each. After the suspension settled, 2 mL of solution was removed and placed in a 2 mL GC vial. The solutions were then analysed using a HP Gas Chromatograph (GC) with a Flame Ionization Detector (FID). The calibration curve was based on a 10 point concentration system.

RESULTS AND DISCUSSION

The calibration curve shown in Figure 2 was created using 10 standards of concentrations of 1-1000ppm (synthetic gasoline in solvent). The resulting calibration equation is as follows:

$$C = GC \text{ Area} / 4222.8$$

where

C = concentration (mass synthetic gasoline * 10⁶ / mass solvent)

$GC \text{ Area}$ = dimensionless quantity provided by the integration tool in the HP Labs suite.

As seen in Figure 2, the calibration curve had an excellent correlation coefficient of $r^2 = 0.981$. Using the calibration curve, the concentration of synthetic gasoline in each soil sample was collected. The results are given in Table 1 and Table 2. Review of the data shows a general decrease in concentration over time as expected, confirming the expected loss through volatilization and degradation.

Figures 3 and 4 show the relationship of concentration in soil versus time. The declining trend was fit with an exponential regression curve. The resulting first order decay constants are 0.064 d⁻¹ for Delhi soil, and 0.047 d⁻¹ for Elora soil. It should be noted that two visual outliers were removed for the 7th d sample for Delhi and 10th d sample for Elora. The corresponding concentrations had extremely high concentrations relative to the concentrations before and after, indicating experimental error.

Comparing the degradation profile obtained in this study to those determined previously [1][2], indicates that there is a noticeable difference in the behaviour of the synthetic gasoline concentrations. High soil concentrations (2000-4000 mg/kg soil) were not sustained, but instead a sharp decrease occurred to significantly lower the concentrations (0-2 mg/kg). The major difference from previous experiments was the change from a closed glass system to a perforated metal reactor. The perforated reactors were used to better simulate bioventing conditions in the field, where radial gas exchange was induced by the low flow vacuum pumps. It is expected that this causes initial high volatilization before the degradation processes take over. Subsequent tests will be needed to define the

Figure 2. Gas chromatograph calibration curve

Figure 3. Biodegradation for Delhi soil

magnitude of volatilization. Review of experiments completed by Patros [3] using similar perforated reactors, showed a significant loss due to volatilization of about 38-23 mg/kg soil/day for the first 5 days of experimentation. This is consistent with the pattern observed here and should be further investigated.

Previous work by Evyazi determined a universal degradation correlation between soil properties and first order decay constants [2]. This correlation, shown below, comes from experiments performed in glass reactors holding approximately 150 g of soil.

$$\ln(k) = 2.803 * PDP + 0.210 * Sand + 4.886 * OM \\ - 0.094 * Clay - 0.004 * (SW * Sand) \\ - 0.021 * (Sand * PDP) - 0.632 * (OM * PDP) \\ + 0.004 * (SW * Clay) - 23.4997$$

where

k = first order decay constant (d^{-1})
 PDP = petroleum degrader population ($cfu \cdot g^{-1}$)
 OM = organic matter (%)
 SW = soil moisture content (%)
 $Sand$ = ratio of the mass of sand relative to the total mass of soil (%)
 $Clay$ = ratio of the mass of clay relative to the total mass of soil (%)

Using the soil properties and conditions of the experiment performed in the 4 kg perforated metal reactors, inserting them into the degradation correlation, gave k values of $0.17 d^{-1}$ for Delhi, and $0.054 d^{-1}$ for Elora. Comparing these degradation values to the experimental values, it was seen in both soils that scaling up the size of the reactor reduced the biodegradation rate. Sandy soils, however, displayed a much larger vulnerability to differences in reactor size. One possibility is the difference in volume of soil/surface area, where greater the ratio, easier the transfer of air (oxygen) [5]. The larger volume of soil/surface area ratio for the Delhi soil

Figure 4. Biodegradation for Elora soil

allows for improved oxygen transfer for the microbes, it also can increase the rate of volatilization. Further research is required to explore this trend.

Further comparison of the degradation rates allows calculation of a scale up factor (4 kg Experimental k / 150g Correlation k), giving 0.37 for Delhi and 0.87 for Elora. These values suggest that as the reactor size increases, the bioremediation rate will decline. Further work is required with more soils and different sized reactors to determine the applicable degradation rate for transfer laboratory data to the field.

CONCLUSIONS

Mesoscale reactors were used to determine the scale up factor for in-situ bioventing. The first order rate constants obtained from these 4 kg soil reactors when compared to the results from 150 g reactors using similar soil types and contaminant concentrations, gave scale-up factors of 0.37 and 0.87 for Delhi and Elora soil respectively. The actual decay rates were $0.064 d^{-1}$ for Delhi soil, and $0.047 d^{-1}$ Elora soil. These preliminary results indicate a smaller scale up factor for sandy soils (Delhi), than for clayey soils (Elora), which is consistent with Delhi being a more sandy soil. It was also observed that the degradation rate decreased as reactor size increased, leading to a slower decay of synthetic gasoline. This suggests that conservative estimates are needed when transferring lab results to the field.

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