Fm 186-2 Treated Wipers in a Simulated MSW Landfill

A study on biodegradation in an anaerobic environment

Environmental Chemical Solutions

BIODEGRADATION OF TOTAL PETROLEUM HYDROCARBONS IN ADSORBENT PADS UNDER SIMULATED LANDFILL CONDITIONS

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INTRODUCTION

Environmental Chemical Solutions, Inc. (ECS) has developed a product that can be applied to waste or spilled hydrocarbons to immobilize chemicals onto an adsorbent. The adsorbent consists of solid material, which is essentially a pad. Following treatment, the material would be disposed of via a landfill as non-hazardous waste. ECS is interested in assessing whether the encapsulated hydrocarbon contaminants (specifically total petroleum hydrocarbons [TPH]) may be subject to biodegradation within a landfill. The Center for Environmental Microbiology (CEM) conducted a series of laboratory microcosm studies to investigate whether TPH encapsulated on the adsorbent during spill cleanup has the potential to biodegrade within a landfill. This included a demonstration of technology verifying reduction in concentration of Diesel-Range Organics (ORO) and Gasoline-Range Organics (GRO) relative to a control under representative landfill conditions. The following report provides a description of standardized methodologies, results, and interpretations of the data, as well as recommendations. For ease in presentation, the data is summarized as appropriate in table or figure format within the report. Detailed data/results sheets are provided in Appendix A.

MATERIALS AND METHODS

Initial Assessment Study

ECS provided a protocol for CEM to follow to simulate exact conditions relative to the use of ECS's product. ECS provided written and electronic training to CEM concerning cleanup procedures of fuel spills. Fuel was spilled on-site at CEM and CEM personnel followed the ECS protocol for cleanup. Immediately following the clean up procedure, both the diesel contaminated pad and the gasoline contaminated pad were analyzed for ignitability of solids by EPA Method 1030, and the gasoline contaminated pad was additionally analyzed for benzene by EPA Method 8260. Two independent biodegradation studies were then conducted using the diesel fuel and premium unleaded gasoline pads.

Baseline Characterization

In accordance with the ECS protocol, a spill and cleanup procedure was conducted on-site with diesel fuel and premium gasoline (91 octane). Each spill was sprayed with a proprietary ECS chemical, mixed as directed, and wiped with the ECS pad. CEM heavily saturated both pads with the resulting solution to attain an even saturation throughout the pad to monitor biodegradation.The pads were then sent to an independent lab and tested for hazardous waste characteristics as described above.

Degradation Study (Microcosm Study)

Thereafter, pieces of the used pad were placed within 40-mL microcosm vials to which moist garden soil was added. Control vials contained the used pad without soil treatments. All treatments were conducted in duplicate. Microcosms were set up such that a set was sacrificed each sampling event to prevent hydrocarbon losses due to volatilization. A set of vials were sampled immediately (T=O) and analyzed for concentrations of DRO arid GRO by gas chromatography/mass spectrometry (GC/MS) using EPA Method 8015B by an accredited laboratory. Three additional sampling events were conducted at weeks 1, 2 and 4.

RESULTS AND DISCUSSION

Initial Assessment Study

Results of initial assessment studies are presented in Table 1 below.

Table I. Results of initial assessment studies.

Treatment	Method of Analysis	Result
Diesel Contaminated Pad	1030 Ignitability	Pass
Gasoline Contaminated Pad	1030 Ignitability	Pass
Gasoline Contaminated Pad	8260 Benzene	Not Detected

The ignitability of solids in the initial assessment study was conducted to determine if combustion would propagate from the used pad within a specified period of time. Results showed that the used pads for gasoline and diesel spill clean up did not propagate combustion (Table 1). The gasoline contaminated pad was analyzed for benzene by EPA Method 8260 and benzene was not detected (reporting limit of 0.001 mg/Kg).

Degradation Study (Microcosm Study)

Results of the initial microcosm study are shown in Tables 2 and 3 for Diesel and Gasoline Range Organics, respectively.

Table 2. DRO degradation microcosm study results

	Control (non-enriched pad)		Treated pad enriched with soil)	
	ORO (mg/Kg)	Reporting Limit (ma/Kg)	ORO (mg/Kg)	Reporting Limit (mg/Kg)
T=O week	440,000	1,000	5,250/15,000*	10/100*
T=1 week	420,000	1,000	20,500	100
T=2 weeks	450,000	1,000	14,500	100
T=4 weeks	460,000	1,000	9,600	100

*Initial results for TPH concentration of the treated ORO at T=O was significantly lower than that of T=l. The discrepancy can be attributed to inherent variability of diesel distribution on the pad or strong initial emulsification effect of the ECS surfactant. Therefore, T=O was repeated and the results shown in Table 2 reflect the new data.

Table 3 GRO degradation microcosm study results

	Control (non-enriched pad)		Treated (pad enriched with soil)	
	GRO (mg/Kg)	Reporting Limit (mg/Kg)	GRO (mg/Kg)	Reporting Limit (mg/Kg)
T=O week	9,950	500	165	25
T=1 week	12,500	500	94	25
T=2 weeks	9,650	500	75	25
T=4 weeks	11,500	500	102	25

The decrease in TPH concentration in the soil microcosms relative to the controls provides reliable evidence of biodegradation of the petroleum hydrocarbons under simulated (methanogenic) landfill conditions (Tables 2 and 3).

Conclusions

This biodegradation study was conducted to provide preliminary evidence of hydrocarbon degradation in the ECS pads (reduction in concentration relative to a control) under simulated landfill conditions. For this study, TPH was specifically assessed based on regulatory considerations and prior testing. We demonstrated biodegradation of TPH in used pads under simulated landfill conditions. In summary, the following results were observed:

i) Review of the training material and subsequent testing seems to indicate that the fuel treated pad does not exhibit the hazardous waste characteristics of toxicity (TCLP Benzene) or ignitability (1030 ignitability of solids).

ii) Concentrations of hydrocarbons decreased substantially in the ECS pad subjected to the simulated landfill conditions relative to the control, demonstrating degradation of petroleum hydrocarbons in the pad under simulated landfill conditions. The concentrations of hydrocarbons in the control stayed relatively stable indicating that there were no volatilization losses and that true biodegradation had occurred in the microcosm treatment.

iii) At week 4, the rate of degradation, however slowed down which can be expected due to limited carbon supply as a result of the rapid decrease in concentration of TPH.

iv) Apparent differences in concentrations of hydrocarbons in the microcosm treatments for gasoline and diesel fuel compared to the untreated control for the sampling time (T = 0 week) can be attributed to degradation due to rapid activity of soil microbial enzymes and possible sorption to organic matter.

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Biodegradation of Benzene in Adsorbent Pads Under Simulated Landfill Conditions

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Revision 0

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INTRODUCTION

Environmental Chemical Solutions, Inc. (ECS) has developed a proprietary process in which a chemical product is applied to waste or spilled hydrocarbons (gasoline, etc.), following which the chemical/hydrocarbon mixture is wiped up and immobilized within an adsorbent pad. Following treatment, the pad is expected to be disposed of via a landfill as non-hazardous waste. ECS is interested in assessing whether the hydrocarbon contaminants (specifically benzene) encapsulated within the pad may be subject to biodegradation under landfill conditions. A bench-scale treatability study was thus conducted at the Center for Environmental Microbiology (CEM) to investigate whether benzene contained within the adsorbent pad has the potential to biodegrade within a landfill without the addition of biostimulating agents. The stated goal of the study was thus as follows:

> Provide preliminary evidence of hydrocarbon degradation in the pad (reduction in concentration relative to a control) under simulated landfill (methanogenic) conditions.

The following report provides a description of standardized methodologies, results, and interpretations of the data, as well as recommendations. For ease in presentation, the data is summarized as appropriate in table format within the report. All data/results sheets are provided in Appendix A.

MATERIALS AND METHODS

Initial Benzene Recovery Studies

An initial study was carried out to determine whether benzene could be extracted from the pad and measured at concentrations relevant to assessing removal. In accordance with the ECS protocol, a spill and cleanup procedure was conducted on-site with regular gasoline. The pad was then analyzed by an accredited laboratory using the toxic characteristic leaching procedure (TCLP). Through EPA Method 8260, the pad yielded only 2.0 µg/L of benzene, and this level was determined to be too low to yield meaningful results in quantifying degradation under methanogenic conditions in a laboratory experiment. CEM was thus provided with a clean pad for the study. Aliquots of the clean pad were treated with a mixture (1:1) of gasoline and the proprietary ECS chemical used in the cleanup process, and placed within 40 mL microcosm vials. In addition, pure benzene was spiked into additional pad samples at a concentration of 2630 mg/Kg, and placed in microcosm vials. Furthermore, aliquots of the clean pad were treated with a mixture of gasoline, the proprietary ECS chemical and moist soil, and placed within 40 mL microcosm vials. All treatments were conducted in duplicate. Each vial was extracted with methanol, and benzene was measured using gas chromatography/mass spectrometry (GC/MS) using EPA Method 8260 by an accredited laboratory.

Microcosm Study

The material was soaked in a 1:1 mixture of gasoline and ESC chemical, and dispensed into 40-mL glass bottles with permeable septa in duplicate. Based on results from the initial recovery study, benzene was spiked to artificially raise concentrations to allow for more accurate tracking of contaminant trends.

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Treatments were as follows:

1. No additions (control)
2. Incubated in fresh, moist soil

Microcosms were set up such that a set was sacrificed each sampling event to prevent hydrocarbon losses due to volatilization. Microcosms were flushed with ambient air which contains oxygen and carbon dioxide to simulate landfill conditions to the extent possible (i.e. O_2 respiration followed by methanogenesis) and sealed following set-up. A set of vials were sampled immediately (t = 0), and periodically thereafter, and analyzed for benzene (GC/MS) and methane gas chromatography/flame ionization detector (GC/FID). Two additional sampling events were conducted at intervals of 2 weeks.

RESULTS AND DISCUSSION

Initial Benzene Recovery Studies

Results of the initial benzene recovery studies are presented in Table 1.

Table 1. Results of initial benzene recovery studies.

Treatment	Spike Amount (mg/Kg)	Result (mg/Kg)	%Recovery
Gas + Chemical	N/A	11.1	N/A
Spiked Pad	2630	2250	86

The initial benzene recovery studies were conducted to ensure that benzene could be extracted from the pad using methanol as a solvent. Prior studies conducted independently by ECS had indicated that the benzene was tightly retained within the pad. This was confirmed by TCLP analysis on the used pad, which yielded a result of 2µg/L. Based on this study, it was determined that benzene could effectively be extracted from the pad which was soaked in the gas/chemical mixture. However, the unspiked result was only 11.1 mg/Kg, and thus it was determined that additional benzene would be added to the pad to give a higher concentration to better meet the goal of tracking benzene disappearance.

Microcosm Study

Results of the initial microcosm study are presented in Table 2.

Table 2. Microcosm study results.

	Treated (pad inoculated with soil)		Control (uninoculated pad)	
	Benzene (mg/Kg)	Methane (mg/L)	Benzene (mg/Kg)	Methane (mg/L)
T=0 weeks	545	17	1,200	16.5
T=2 weeks	71	230	1,015	17
T=4 weeks	97	1,250	1,100	16.5(0.7)

The following observations are apparent:

Concentrations decreased substantially in the pad subjected to the simulated landfill conditions relative to the control (82% removal observed). The fact

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that benzene levels were lower at T=0 in the treated pad relative to the control is attributed to sorption of benzene by soils. This was verified experimentally in a side experiment in which benzene was spiked (at the same concentration) into a set of vials containing soil only. The benzene concentration in the soil only sample was 450 mg/Kg, which is reasonably similar to the benzene concentration in the pad + soil at T=0 of 545 mg/Kg (Table 2).

Methane concentration in the treated sample clearly increased relative to the control, demonstrating degradation of petroleum hydrocarbons in the pad under simulated landfill conditions.

CONCLUSIONS AND RECOMMENDATIONS

This bench-scale treatability study was conducted to provide preliminary evidence of hydrocarbon degradation in the pad (reduction in concentration relative to a control) under simulated landfill conditions. For this study, benzene was specifically assessed based on regulatory considerations and prior testing. It is well known that petroleum hydrocarbons in the gasoline range are biodegradable, and thus if benzene degradation can be demonstrated, it can be assumed that other constituents would degrade as well. Methane is a byproduct of biodegradation of organic contaminants under anaerobic (landfill) conditions. Methane production was also tracked, thus providing two lines of evidence for petroleum degradation under typical landfill conditions.

Thus, two lines of evidence were explored in preliminarily demonstrating biodegradation of benzene in the pad under simulated landfill conditions. The relative increased methane concentration in the inoculated treatment provides evidence of biodegradation of the petroleum hydrocarbons under methanogenic conditions. Decreases in benzene levels in the inoculated treatments relative to the control also provide evidence of biodegradation. These results show that biodegradation of benzene (and thus other petroleum hydrocarbons in the gasoline range), are subject to biodegradation in the spent ECS pads under landfill conditions.

*Petroleum waste is a presumptive hazardous waste and the users/generators are responsible for proper waste characterization and disposal. Regulations establish that prior knowledge of the waste and the treatment process in which it was generated can be applied in determining a waste's classification. The FM 186 program is an immediate response spill treatment procedure that can be applied as part of prior knowledge in which the waste was generated. Federal and state regulations state that generators shall determine their waste classification and dispose of it correctly. Nothing herein is to be taken as approvals that all spill materials would be rendered non-hazardous.

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