Biodegradation of Benzene in Adsorbent Pads Under Simulated Landfill Conditions

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Revision 0

Prepared For:

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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 f.l.g/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.
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. O₂ 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.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Spike Amount (mg/Kg)</th>
<th>Result (mg/Kg)</th>
<th>%Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas + Chemical</td>
<td>N/A</td>
<td>11.1</td>
<td>N/A</td>
</tr>
<tr>
<td>Spiked Pad</td>
<td>26.50</td>
<td>2250</td>
<td>86</td>
</tr>
</tbody>
</table>

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 211g/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.

<table>
<thead>
<tr>
<th>T=0 weeks</th>
<th>T=2 weeks</th>
<th>T=4 weeks</th>
<th>T=0 weeks</th>
<th>T=2 weeks</th>
<th>T=4 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene (mg/Kg)</td>
<td>545</td>
<td>71</td>
<td>97</td>
<td>1,200</td>
<td>1,100</td>
</tr>
<tr>
<td>Methane (mg/L)</td>
<td>17</td>
<td>230</td>
<td>1,250</td>
<td>1,200</td>
<td>1,100</td>
</tr>
</tbody>
</table>

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
that benzene levels were lower at T=O 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=O 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.