Separation of Petroleum Hydrocarbons from Soil and Groundwater through Enhanced Bioremediation

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In this study, enhanced air biosparging techniques were investigated for remediating VOC-contaminated subsurface. Desired injection manners were acquired through batch- and bench-scale experiments in order to reduce the operating costs, eliminate the need for off-gas treatment, and enhance the efficiency of contaminant removal. The fate of benzene in water and water-soil systems under a variety of conditions was examined. Blank experiments were conducted to compare the efficiencies of different enhancement measures in promoting biodegradation. The effects of soil properties and injection manners on benzene removal were investigated through a number of experimental runs. The results indicated that using pulsed air injection in an air biosparging system could significantly reduce benzene concentration in both the pure fine-sand-without-clay system and the system with 95% fine sand and 5% clay. The rates of aerobic biodegradation for benzene in both water and water-soil systems were generally high in the study systems. Also, the effect of clay content (in fine sand) on benzene removal is significant at low air flow rate. The removal efficiency generally decreases with the increase of clay content.

Keywords: bioremediation, groundwater, hydrocarbon, petroleum, separation, soil, sparging, volatile organic compounds

Air sparging, a technique that uses the injection of a gas into the subsurface, is an effective method for remediating soil and groundwater contaminated by volatile organic compounds (VOCs), particularly dissolved petroleum hydrocarbons (Marley et al., 1992;...
Reddy, 1996; Maqsood et al., 2004). The air sparging attenuates organic compounds dissolved in subsurface through two mechanisms: physical stripping (volatilization) as air moves through the aquifer and aerobic biodegradation of VOCs through increased oxygen supply (Johnson et al., 1993). Some analyses have emphasized the advantages of air sparging for delivering oxygen below the water table for aerobic biodegradation (Symons et al., 1995), while the biodegradation is considered as an important adjunct for semi-volatile and even non-volatile compounds (Marley and Li, 1994). The process studies that assessed the contribution of volatilization and aerobic degradation to overall effectiveness of air sparging have also been conducted (Johnson, 1998, 1999).

Most previous process studies have focussed on movement and distribution of air through the aquifer in laboratory models (Ji et al., 1993; Liu et al., 2003; Maqsood et al., 2004) and in the field (Johnson et al., 1997). Laboratory studies have also been performed to investigate air flow patterns and to evaluate the removal rates of toluene in both gravel and sand (Semer et al., 1996; Semer and Reddy, 1998). The results from the previous laboratory investigations on air sparing process have helped to understand air flow patterns in saturated soils (Ji et al., 1993).

However, these studies were carried out at relatively high air flow rates. The high flow rate, in some cases, would increase the contaminant volatilization, but the costs of air injection and of above ground off-gas recovery would also be significantly increased. Some proponents have advocated biosparging, which aims to minimize volatilization in relation to biodegradation (Billings et al., 1994; Clarke et al., 1996; Javanmardian et al., 1995; Weymann, 1995). However, the effects of system variables—particularly the soil type, the manner of air injection, and the species of microorganism—on the removal efficiency have not been systematically investigated.

In fact, soil compositions in many contaminated sites could be complicated with various contents of sand and clay. The clay content could directly affect soil permeability, resulting in impacts on contaminant transport (in both liquid and gaseous phases) in subsurface. Consequently, the effectiveness of contaminant removal through air-sparging enhanced volatilization would be affected. One of the tasks in this study is to investigate the effect of the clay content on contaminant removal (Huang et al., 2004).

Another issue to be addressed in this study is to examine the effect of pulsed air injection (with low airflow rate) on the contaminant removal. A system with low airflow rate and pulsed air injection will have significantly lower operating cost than that with high airflow and continuous injection. Development for such a more cost-effective system is desired if its efficiency is satisfactory. The pulsed air injection involves the use of a cyclic injection regime: injection, idle, injection again, idle again, and so on; the process will repeat throughout the remediation process.

**Experimental Methodology**

**Experimental Set-up**

A one-dimensional apparatus consisting of a Plexiglas column 24 cm in height and 2 cm in diameter was used for the testing. A schematic of this apparatus is shown in Figure 1. After the top stopper was moved, the test soil was carefully placed into the column. The top stopper was then secured to the column. The stopper is made of rubber to prevent any VOC leakage to the atmosphere. The bottom of the column consisted of an injection grid and a port fitted with two-way connector. The grid ensured a uniform injection pattern across section of the soil. A gravel filter was placed directly above the injection
grid to further ensure uniform injection and also to prevent the tested soil from clogging the injection grid. One way of the two-way connector was used for nutrient injection. The second way was used for air injection. The injected air migrated upward through the soil column, eventually reaching the top of the column, where it exited through an effluent tube.

**Materials**

To determine the effect of clay content on the efficiency of an air sparging system, four kinds of clean soils were considered. They were fine sands with 0%, 3%, 5%, and 10% of clay, respectively. The particles of fine sand were passed through a #60 U.S.A. standard sieve, and those of clay were passed through a #100 U.S.A. standard sieve. Thus, the particle sizes of fine sand and clay were below 0.25 mm and 0.15 mm, respectively.

Gasoline was chosen as the contaminant for all tests and was purchased from a commercial gas station. To simulate the contaminated groundwater, a combination of gasoline and water was added into a 1000-mL glass bottle with seal screw-cap, letting the water saturated with gasoline. Then this combined gasoline-water was used as the contaminated water sample.

**Microorganism Adaptation and Incubation**

Microbial samples were collected from a wastewater treatment plant. After sedimentation of flocculants for over two hours, the supernatant of microbial suspension was used as
inoculum and was then added into a 4-L basal medium with 150 mg/kg NH$_2$CONH$_2$ and 50 mg/kg K$_2$HPO$_4$. The bottle containing basal medium, inoculum and gasoline was sparged with air. The gasoline concentration was increased slowly during the course till the concentration of benzene in the basal medium reached 200 ppm. In the basal medium, the aerobic microorganisms were enriched and could be grown and become acclimated to gasoline.

**Experimental, Sampling and Analytical Methods**

**Batch Biodegradation Studies.** To study the biodegradation process of benzene in water and sand-water systems, three experiments were conducted. The specific procedures used in these experiments were as follows:

1. For the soil test, soil was first placed to the reactors (glass bottles);
2. Microbial cultures were inoculated into the bottles. Then each bottle was capped with a sleeve stopper;
3. Using a 5.0-mL-capacity syringe, a portion of gasoline contaminated water was placed in other glass bottles;
4. Using a 5.0-mL-capacity syringe, an appropriate amount of water was added into each bottle containing the contaminated water to dilute it to a desired concentration;
5. Reaction bottles were shaken continuously on a shaker.

To prevent any VOCs leakage and for the convenience of obtaining samples, the bottle was capped with sleeve stopper, which can be easily perforated with hypodermic needles. Immediately after inoculation, the gas in the headspace of bottle was taken as the initial (hour-zero) sample to determine the initial contaminant concentration. The gas was then sampled at several later time stages to monitor the concentrations and the removal efficiencies. These samples were analyzed using gas chromatography (GC).

**Bench-Scale Air Biosparging Studies.** The clean soils were mixed thoroughly with proper amounts of contaminated water and microbial culture. The packing for the study column was performed carefully by transferring the slurry layer by layer to minimize trapped air bubbles in the saturated media. The packing process was completed within 10 minutes, and efforts were made to minimize volatilization of VOCs. Immediately after the packing, the column was sealed by closing tightly the stoppers and the influent and effluent tubing. After the determination of the initial contaminant concentration, the air injection process would begin. The injected airflow was maintained at 8 mL/min, and the temperature was kept at 22 ± 2°C (Howe et al., 2003).

Samples for the initial contaminant concentrations within the soil column were obtained from the column's sampling point, right after the soil had been loaded into the column. Water samples were then obtained at different time intervals to monitor dynamic variations of contaminant concentrations and removal efficiencies. The reproducibility of the tests was verified by performing selected duplicate tests under identical conditions.

A Varian model CP-3800 gas chromatograph (GC) equipped with a flame ionization detector (FID), a photo ionization detector (PID), and a Chrompack WCOT fused silica 0.53 mm × 30 m capillary column was used for analyzing contaminant contents in all gaseous and water samples. The GC was controlled by a Varian computer system. The initial oven temperature was programmed at 65°C. From 65°C, the oven temperature was increased to 135°C at a rate of 10°C per minute. The oven temperature was held
Table 1
Conditions for blank tests

<table>
<thead>
<tr>
<th>Test no.</th>
<th>Volume of sludge added (mL)</th>
<th>Soil</th>
<th>Air venting time (min/12 hrs)</th>
<th>Concentration of gasoline (ppm)</th>
<th>pH</th>
<th>Concentration of nutrient (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 4</td>
<td>0</td>
<td>N</td>
<td>0</td>
<td>104</td>
<td>6.5</td>
<td>0</td>
</tr>
<tr>
<td>Run 5</td>
<td>10</td>
<td>N</td>
<td>0</td>
<td>108</td>
<td>6.5</td>
<td>10</td>
</tr>
<tr>
<td>Run 6</td>
<td>0</td>
<td>N</td>
<td>20</td>
<td>99</td>
<td>6.5</td>
<td>0</td>
</tr>
<tr>
<td>Run 7</td>
<td>10</td>
<td>N</td>
<td>20</td>
<td>107</td>
<td>6.5</td>
<td>10</td>
</tr>
</tbody>
</table>

N 100% fine sand (passed through #60 U.S.A. standard testing sieve).

for 5 minutes and temperatures of the injector port and the detector were maintained at 250°C and 200°C, respectively. Helium, at an initial flow of 5.5 mL per minute, served as the carrier gas.

Results and Discussion

Batch Biodegradation Study

To study the biodegradation process of benzene, three batch experimental runs were conducted. Run 1 was conducted in the water with 1 mL of microbial cultures and 5.49 ppm initial benzene concentration. Run 2 was also conducted in the water with 1 mL of microbial cultures but with 2.97 ppm initial benzene concentration. Run 3 was conducted in a sand-water system, with 1 mL of microbial cultures and 2.97 ppm benzene concentration. Thus, Runs 1 and 2 were carried out to determine the effect of contaminant concentration on biodegradation rate, while Run 3 was to examine biodegradation of benzene in a sand-water system.

Blank Test

For determination of the efficiency of the bench-scale column system, four blank runs were conducted. The testing conditions are shown in Table 1. The soil type, pH, and contaminant level in these systems are identical. The differences among them are:

- Run 4 was conducted under natural conditions, i.e., no additional microorganism, oxygen or nutrient was introduced into the column;
- Run 5 was conducted with additions of microorganisms and nutrients, but without additional oxygen;
- Run 6 was conducted by pulsing air injection to enhance the biodegradation; and
- Run 7 was conducted with not only additional microorganisms and nutrients, but also pulsed air injection.

The results of the above four sets of experiments are presented in Figure 2. It is indicated that the four experimental degradation curves are different from each other due to the varied testing conditions. The Run 4, which was conducted under natural conditions, had the lowest degradation rate. The benzene removal rate in Run 4 was below
The benzene removal rate in Run 5 was about 36% after 120 hours of treatment. Although the biodegradation rate of Run 5 was enhanced by adding microorganisms and nutrients and was about two times that of the Run 4, this degradation rate was still low. By injecting pulsed air into the column (in Run 6), the biodegradation rate was increased. The benzene removal rate in Run 6 was about 56% after 130 hours of treatment, which was higher than those of Runs 4 and 5 were. In comparison, Run 7 was enhanced by adding microorganisms, nutrients and injecting pulsed air, leading to a much higher degradation rate. The benzene removal rate was over 96% after 93 hours of treatment.

The results of the blank tests clearly indicate that introducing the microorganisms and nutrients can enhance the benzene degradation. But the enhancement efficiency was still low, and may not meet the requirement to treat a site in a short period of time with a lower cost. Injecting the pulsed air can enhance the biodegradation rate more effectively. This is mainly because aerobic biodegradation is often limited by availability of oxygen (Thomas and Ward, 1992; Litchfield, 1993; Dupont, 1993; Baker et al., 1994). Significantly increase degradation rate can be obtained when microorganisms, nutrients, and pulsing air were all introduced to the system.

**Effect of Clay Content**

To examine the effect of clay content (in soil) on the biodegradation process, four runs were conducted for four soil types which were composed of fine sand as well as 0%, 3%, 5% and 10% of clay, respectively. A pulsed air injection option was adopted (i.e., 20 minutes of injection duration, followed by 700 minutes of idle period). Testing conditions of these four runs are given in Table 2.

Figure 3 shows a plot of benzene concentrations versus elapsed times in the four kinds of soils. It indicated that benzene concentrations significantly decreased with elapsed time, demonstrating effectiveness of the designed remediation systems. However, differences exist among the four soil types: the lower clay content, the higher removal rate. For the column with pure fine sand (without clay), the benzene removal rate was over 98% after
Table 2
Test conditions for Run 8 to Run 11

<table>
<thead>
<tr>
<th>Test no.</th>
<th>Volume of sludge added (mL)</th>
<th>Clay content (%)</th>
<th>Air venting time (min/12 hrs)</th>
<th>Concentration of gasoline (ppm)</th>
<th>pH</th>
<th>Concentration of nutrient (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 8</td>
<td>20</td>
<td>0</td>
<td>20</td>
<td>113</td>
<td>7.7</td>
<td>100 40</td>
</tr>
<tr>
<td>Run 9</td>
<td>20</td>
<td>3</td>
<td>20</td>
<td>116</td>
<td>7.7</td>
<td>100 40</td>
</tr>
<tr>
<td>Run 10</td>
<td>20</td>
<td>5</td>
<td>20</td>
<td>107</td>
<td>7.7</td>
<td>100 40</td>
</tr>
<tr>
<td>Run 11</td>
<td>20</td>
<td>10</td>
<td>20</td>
<td>105</td>
<td>7.7</td>
<td>100 40</td>
</tr>
</tbody>
</table>

Figure 3. Effect of clay content.

84 hours of treatment. In comparison, the column with 10% clay has a removal rate of approximately 70% only, even after 147 hours of treatment.

Thus, soil properties have significant impacts on the remediation efficiency. According to Ji et al. (1993) and Johnson et al. (1993), the injected air in saturated porous media usually moves in continuous air channels, with VOCs volatizing across the air-water interface of the air channels into air phase. The following differences exist between coarse and fine media:

1. Normally, more channels were expected to form for coarser materials than for fine ones. This would mean that the distances between the air channels were closer for coarser materials, resulting in a larger volume of subsurface media that would be affected by the air channels.

2. Aqueous diffusion of VOCs would be faster in coarser materials than in fine ones. Consequently, the benzene removal efficiency in coarser materials would be higher than that in fine materials.

3. The more air channels, the more oxygen and nutrients will be held up in the channels during the idle period (when no air injection is provided). This will result in faster biodegradation of benzene.
Effect of Pulsed Air Injection

To study the effect of the pulsed air injection on the remedial efficiency, two sets of tests were performed, with each consisting of three tests. The testing conditions are listed in Table 3.

Figure 4 shows scattered plots of benzene removal rate versus elapsed time in systems packed with pure fine sand (Runs 12, 13, and 14). The three curves are for injection duration of 10, 20, and 40 minutes, respectively. In general, the three curves are quite close to each other, although the test with 40-minute injection duration tends to remove benzene more quickly than the others do. The results demonstrate insignificant impact of the length of injection duration in the pure fine-sand system.

Figure 5 shows scattered plots of benzene removal versus cumulative injection time (i.e., the cumulative duration when the air injection pump is on) for the same three tests (Runs 12, 13, and 14). It indicated that the removal rates under the three injection regimes (i.e., tests with 10-, 20-, and 40-minute pulsed injection duration) are very different from each other. The system with 10-minute pulsed injection duration appeared to be
most effective for benzene removal, where over 96% of benzene were removed within 50 minutes of cumulative operating time; the system with 40-minute pulsed injection period had the lowest efficiency, taking about 240 minutes of cumulative operating time to remove 98% of benzene. These results demonstrate that the increase in the length of pulsed injection duration may make little or no contribution to the benzene removal. This may be because:

1. A very small number of channels were formed in the fine sand that maintained their integrity during the entire testing period. This small number of channels meant that the majority of the benzene had no direct contact with the injected air and had to migrate to the air channels via diffusion, a process that requires much more time than volatilization. So, the amount of benzene removed through volatilization was limited and did not increase with the length of the pulsing injection period after the length reached a certain level.

2. On the other hand, biodegradation may be the most important process for benzene removal in the study system. Oxygen was supplied during air injection, where the shut-down periods allowed biodegradation to occur and to remove the contaminants. When the amount of oxygen required for biodegradation is satisfied, the biodegradation rate would not increase with any additional amount oxygen supply. Under such a condition, any increase in the length of pulsed injection duration would not have significant impact on the benzene removal.

Figure 6 shows the benzene removal versus elapsed time for the three injection regimes in column systems packed with 95% fine sand and 5% clay (Runs 15, 16, and 17). It is indicated that the test with 40-minute injection duration has the highest remedial efficiency, followed by those with 20- and 10-minute injection duration. The trend is that the removal rate increases as the length of pulsed injection duration increases. The results demonstrate significant impact of the injection duration on the benzene removal in the fine sand with clay system.

Figure 7 shows scattered plots of benzene removal versus cumulative injection time (i.e., the cumulative time when the air injection pump is on). It indicated that the removal rates under the three injection regimes (i.e., tests with 10-, 20-, and 40-minute pulsed...
injection duration) are quite similar to each other, although the test with 40-minute pulsed injection duration has somewhat higher efficiency. The curves of 10- and 20-minute pulsed injection duration are quite close to each other.

Figures 5 and 7 show that curves of benzene removal versus cumulative injection time are significantly different between the two testing soils. Figure 7 shows that the benzene removal rate was related to the cumulative injection time in the fine-with-clay-system. Due to the difficulty in establishing a multiple channel network in the fine-sand-with-clay system, the number of channels established in such a system was much fewer than those in the fine-sand-without-clay system. Therefore, in the fine-sand-with-clay system, the supply of oxygen through these few channels would be difficult, and may be affected by the cumulative injection time.

Figures 4 and 6 show that the effect of the pulsed injection duration (10, 20, and 40 min) on benzene removal is more evident in the fine-sand-with-clay system than in the fine-sand-without-clay. In the fine-sand-with-clay system, due to the lack of sufficient channels for delivering oxygen for biological activities, there are still significant demands
on oxygen; the increased injection duration will then supply more oxygen for the system, leading to improved benzene removal rate. In comparison, in the fine-sand-without-clay system, the needed oxygen is generally available, such that the increased oxygen supply is not much appreciated.

Conclusions

Air biosparging is an effective means for remediating VOC-contaminated subsurface. Optimizing injection manners is important in reducing operation costs, reducing or eliminating the need for off-gas treatment, and enhancing the efficiency of contaminant removal. In this study, batch and bench scale experiments were conducted to examine the fate of benzene in water and water-soil systems under a variety of conditions. Blank experiments were conducted to compare the efficiencies of different enhancements in promoting biodegradation. The effects of soil properties and injection manners on benzene removal were investigated through a number of experimental runs. The following conclusions can be drawn based on results from this study:

1. Using pulsed air injection in an air biosparging system can significantly reduce benzene concentration in both the pure fine-sand-without-clay system and the system with 95% fine sand and 5% clay. This could result in reductions in operating costs.
2. The rates of aerobic biodegradation for benzene in both water and water-soil systems are generally high in the study systems.
3. The effect of clay content (in fine sand) on benzene removal is significant at low air flow rate. The removal efficiency generally decreases with the increase of clay content.
4. The effect of the length of pulsed air injection duration (or cumulative air injection time) on benzene removal is insignificant in the pure fine-sand-without-clay system, but is very significant in a system with 95% fine sand and 5% clay.

References


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