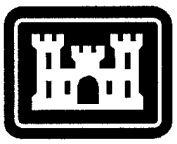

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Fluidized-Bed Adsorption Bioreactor for the Treatment of Groundwater Contaminated with Solvents at Low Concentration

Paul H. Miyares, Cynthia V. Teeter, and C. James Martel January 1999

Abstract: Volatile organic compounds (VOCs) are a major source of water contamination in the U.S. They pose a threat to the environment and are a potential hazard to human health. Trichloroethylene (TCE) is the most common of these pollutants. TCE is usually remediated through pumping and treating it, using either air stripping or granular activated carbon. Bioremediation is an alternative treatment that uses microbes to convert hazardous substances into nonhazardous compounds. A fluidized bed adsorption bioreactor is examined here for the treatment of groundwater contaminated at low concentrations. This pilot study showed that the packed adsorbent bed could be loaded in approximately 36 hours at a flow rate of 120 mL/min. The remediation phase of the process took approximately 13 days. The reduction in the TCE concentration in the sorbent during each round indicated that it was being remediated by the microbiological process. Areas that need to be improved are the rate of remediation and the loading capacity of the adsorption beds. Currently, each complete cycle of loading and remediating requires 2 weeks while only mineralizing 58 mg of TCE per column.

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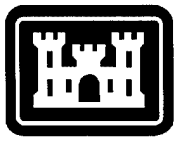

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January 1999

Prepared for
STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM

PREFACE

This report was prepared by Dr. Paul H. Miyares, Research Chemist, Geochemical Sciences Division, U.S. Army Cold Regions Research and Engineering Laboratory, Cynthia V. Teeter, Mechanical Engineer, Environmental Restoration Branch, U.S. Army Waterways Experimental Station, and Dr. C. James Martel, Environmental Engineer, Geochemical Sciences Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this work was provided by the Strategic Environmental Research and Development Program (SERDP).

Technical review of the work reported here was provided by Alan D. Hewitt and Dr. Daniel J. McKay, both of CRREL.

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Fluidized-Bed Adsorption Bioreactor for the Treatment of Groundwater Contaminated with Solvents at Low Concentration

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INTRODUCTION

Background

Volatile organic compounds (VOCs) are a major source of water contamination in the U.S. They pose a threat to the environment and are a potential hazard to human health, having been shown to induce cancer and mutations in animals exposed to parts per billion (ppb) concentrations. The U.S. Environmental Protection Agency (EPA) stated that chlorinated organics are the most frequently reported VOCs and have ranked them number one on the priority pollutants list (Gantzer and Wackett 1991). Large scale production of chlorinated solvents, coupled with years of uncontrolled disposal, has lead to the widespread contamination problem that exists today (Lam 1994).

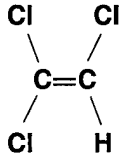


Figure 1. Chemical structure of TCE.

Trichloroethylene (TCE) (Fig. 1) is the most common of these priority pollutants, having been reported at 246 of 1035 Superfund sites (Shannon 1995). Many of the Department of Defense (DOD) and Department of Energy (DOE) sites have reported TCE contamination in the groundwater. TCE is a clear, colorless, nonflammable liquid, whose properties (Table 1) make it an ideal solvent for many industrial processes. TCE has been used an effective degreaser and as a solvent for fats, waxes, resins, oils, rubber, paints, and varnishes. It has been also used as a dry-cleaning solvent and for food extraction, such as in the decaffeination of coffee.

TCE, though, has been shown to induce hepatocellular carcinomas in mice and thus is a suspected human carcinogen (Lam 1994). In response to the potential for human health effects, the U.S. EPA has set limits for a maximum TCE contaminant level in drinking water supplies at 5 ppb.

Commercially available technologies for treatment of environmental contamination by VOCs include recycle–reclamation, thermal incineration, vapor extraction, and bioremediation. Recycle–reclamation involves treatment of spent solvents either on or off site. This minimizes waste handling as well as production through the reuse of re-

Table. 1. Physical properties of TCE (after Fares 1994).

Property	*Value*	*Units*
Formula	C_2HCl_3	
Molecular weight	131.39	g/mol
Density (at 20°C)	1.46	g/cm^3
Vapor pressure (at 20°C)	58	torr
Freezing point	–86.8	°C
Melting point	–70	°C
Boiling point	86.7	°C
Flash point	89.6	°C
Auto ignition temperature	420	°C
Physical state (at 15°C and 1 atm)	Liquid	
Liquid surface tension (at 20°C)	0.0293	N/m
Vapor specific gravity	4.5	g/cm^3
Ratio of specific heats of vapor	1.116	
Latent heat of vaporization	2.4×10^5	J/kg
Viscosity	0.57	cP

claimed material. Rotary kiln incinerators and circulating bed combustion incinerators are common types of thermal treatment (Gerace-Coles 1991). Vapor extraction technologies use an air stream to remove dissolved molecules from liquids. The volatile compounds are trapped out of the air stream using an adsorptive material such as carbon, which is then treated by incineration. Most commonly, TCE is remediated through pumping and treating it, using either air stripping or granular activated carbon. These technologies are very expensive, costing $1 to $5 per 1000 gallons (3785 L) of groundwater.

Bioremediation, using either bioreactors or bioslurries, has been examined as an alternative to incineration. Bioremediation utilizes microbes to convert hazardous substances into nonhazardous compounds. The microorganism uses the contaminant as a carbon source and ultimately converts it to CO_2 and water.

Bioreactors are large vessels in which either contaminated soils or groundwater are treated. The process allows for rapid bacterial growth, which results in maximum degradation rates. The system is made optimal for a given contaminant and type of microorganism, and can be operated under either aerobic or anaerobic conditions. Once the contaminated soil or water has been remediated, it can be returned to its original site as a recovered resource.

Bioslurry treatment of soils is a relatively new remediation technology. It is a reconfiguration of other more widely used biotreatment technologies, such as landfarming and composting. In this method, the contaminated soil is mixed with water and other additives in a reactor to form a slurry. It is similar to other soil and sludge biotreatment technologies in terms of microbiological interactions and contaminant degradation pathways. However, it differs from the other technologies because bioslurry systems substantially increase the rate at which contaminants degrade by increasing the availability of contaminants, electron acceptors, nutrients, and other additives, such as surfactants, to the microbial populations. The result is a biological system that is conducive to optimum microbial activity and increased contaminant degradation rates.

A new bioremediation technology is now being examined for treatment of groundwater contaminated at low concentrations—the fluidized-bed adsorption bioreactor. In this system, groundwater is passed through a packed bed of adsorbent material, such as carbon, carbonaceous resins or, organophilic clays (OPC). When the bed has adsorbed as much as it can, it is put into a closed-loop system with a bioreactor. The bed is fluidized, meaning that fluid is pumped through it at a high flow rate, causing the bed material to become suspended in the solution. As the fluid passes through the bed, it acts as an extractant, removing the contaminants from the adsorbent material. The fluid is cycled through the bioreactor and then back through the packed bed. Once the bed is deemed remediated, more groundwater is pumped through the sorbent and the process starts over.

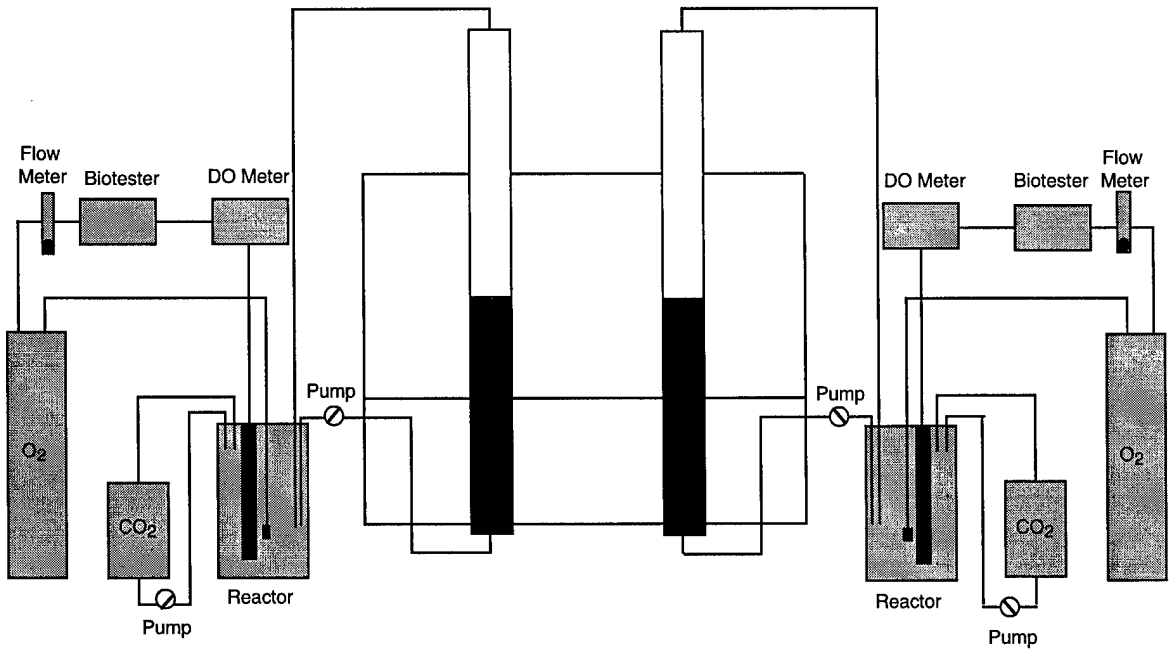


Figure 2. Fluidized-bed adsorption bioreactor.

Such a system was designed at the Waterways Experiment Station (WES) for the treatment of groundwater contaminated with low levels of TCE. Research into the design of this system resulted in the use of an OPC as the sorbent and *Burkholderia cepacia* (G4) as the microbe. This system was optimized at WES using a bench scale model unit. Once optimized, a pilot scale system was designed. Figure 2 shows a schematic of the pilot scale system. The objective of this work was to test and evaluate the pilot scale system and determine its feasibility as a cost effective alternative to current groundwater treatment systems for TCE remediation.

Pilot scale system and operation

The fluidized-bed adsorption bioreactor consisted of a column of an adsorbent material and a bioreactor. The column was a glass tube (10 ft × 2-in. i.d. [3 m × 2-cm i.d.]), packed with 2200 g of an OPC material (Colloid Environmental Technologies Company, Clarion PM-100). The bioreactor consisted of a 10-L glass reactor vessel fitted with a five-port lid, an oxygen supply, a dissolved oxygen probe, a carbon dioxide treatment system, plus the draw and return lines connecting the bioreactor to the column. The microbe used in the reactor was *Burkholderia cepacia* (G4). A biotester (Liquid System Electronic, Model LS/QA) kept the oxygen levels between 5 and 15% of saturation. The carbon dioxide treatment system was a canister in which a 1-M sodium hydroxide was circulated.

The pilot scale system was mounted on two skids (Fig. 3), each having two adsorption columns and the necessary plumbing for loading the columns and providing connections to the bioreactors. The two bioreactors were shared between these skids. A series of peristaltic pumps (Masterflex, Inc.) were used for loading the columns, for circulating with water, for fluidizing the clay bed, and for removing carbon dioxide from the reactors during remediation.

TCE-contaminated groundwater was obtained from a site at CRREL. This is an ideal place to test the methodology. The site is contaminated with TCE only, so results could not be confounded by the presence of other compounds. In addition, it is extremely well characterized; concentrations of TCE in the groundwater are known and are well within the operating limits of the reactors.

The TCE-contaminated groundwater was removed from CRREL well CECRL 11, where the average TCE concentration was 1.52 ± 0.18 mg/L. To load the TCE onto the clay, groundwater was pumped from the monitoring well to a 250-gallon (1137-L) stainless steel holding tank using a bladder pump (Grundfus, Redi-flo2, 2-in.-diameter [5-cm-diameter], submersible pump, located 20 ft [6 m] down the well). Groundwater could not be pumped directly from the well to the columns because the recharge rate of the well was too slow. To maintain a consistent TCE concentration in the water throughout the loading process, as well as to maintain a fairly constant pressure on the loading pumps, the holding tank was kept full. This was done by means of a siphon tube that kept the water level constant.

During the loading process, the groundwater was pumped from the bottom of the holding tank to the base of each pair of columns by means of a peristaltic pump. The flow rate through each column was set at 120 mL/min to allow for maximum loading of the clay in the shortest time period. To ensure that no TCE was loaded while we set the flow rate, distilled water was pumped from a small carboy.

The groundwater was then pumped through the packed clay beds for 48 to 140 hours. Influent and effluent TCE concentrations were determined following the schedule outlined in the *Sample Collection* section. We defined a column to be "loaded" when the ratio of the effluent concentration to the

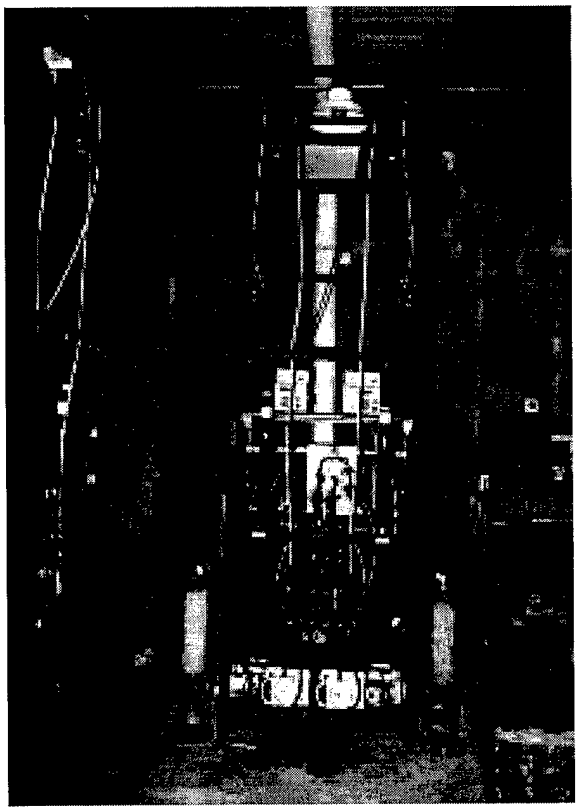


Figure 3. Skid 1 of the pilot scale fluidized-bed adsorption bioreactor system.

influent concentration was greater than 0.85 or when an asymptotic level was maintained for 24 hours. The effluent from the columns was passed through activated carbon canisters and disposed of at CRREL's treatment facility for water contaminated with TCE.

Once loaded, the columns were taken off line and connected to the closed loop system, which included the bioreactors. The bioreators (Fig. 4) contained the G4 microbe in 9 L of a mineral salt solution and 8 g of phenol. The initial phenol concentration in the reactor was 500 mg/L. The clay beds were fluidized by pumping the solution in the bioreactor through the columns at a flow rate of 1.6 L/min. The effluent from the columns flowed back to the bioreaction vessel. Determinations of the TCE concentration in the water and on the clay, as well as the concentrations of the phenol and chloride in the water, were made following the schedule outlined in the *Sample Collection* section. If the concentration of phenol in the water dropped below 60 mg/L, 8 g of phenol was added to the system. The clay material was considered "rejuvenated" when the TCE concentration on the clay was reduced by 75% from the initial concentration.

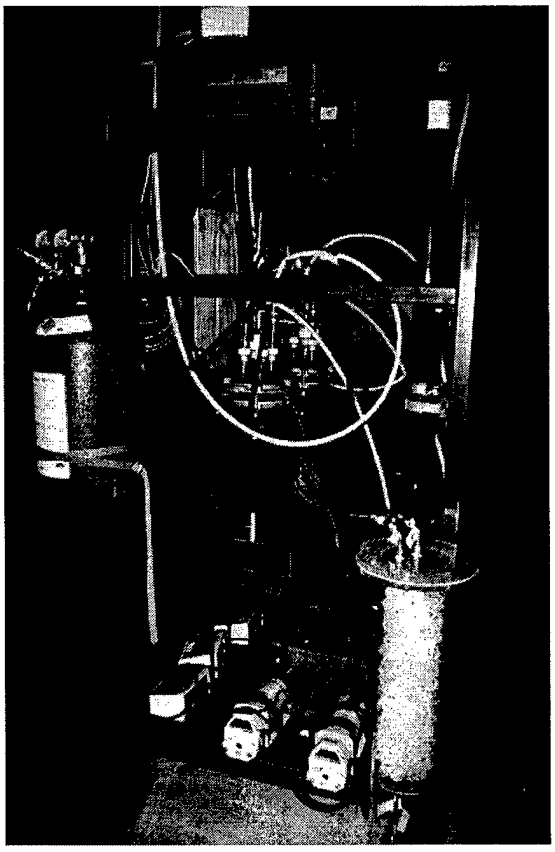


Figure 4. Bioreactor used in the pilot scale study.

In addition to monitoring the system's performance through analyses of clay samples for TCE and water samples for TCE and phenol, we monitored the dissolved oxygen level and metered it to introduce additional oxygen as needed. The system was programmed to add oxygen to 15% of saturation when the level dropped below 5%. Upon determining that the material was rejuvenated, we switched the system back to the loading mode and the bed was reloaded with TCE-contaminated groundwater.

During the pilot study, each column was loaded and remediated three times. One "round" of the study was defined as the loading and rejuvenation of all four columns (i.e., round 1, skid 1 consisted of loading and rejuvenating columns 1 and 2). In addition to monitoring the TCE, phenol, and oxygen concentrations, the system was also monitored for mechanical functioning and performance, including pump maintenance and repair of failed tubing.

The pilot study was run from 9 September to 31 December 1996. The skids were originally enclosed in a wooden framed structure covered with plastic sheeting. Because of a drop in the outside air temperature to below 0°C, the system was moved into a building that was maintained at 4.5°C.

EXPERIMENTAL METHODS

Analysis for TCE

Instrumentation

All of the analyses for TCE were performed using a head space gas chromatography (HS-GC) system composed of the following components:

- An SRI 8610A gas chromatograph equipped with a megabore capillary column, Restek MXT-1 (15 m × 0.53 mm, 5.0-μm film thickness), and a photoionization detector (PID). The carrier gas was He run at a column head pressure of 8.5 lb/in.^{2} (59 kPa).
- A Tekmar 7000 headspace autosampler equipped with a 1.0-mL sampling loop.
- An IBM compatible 386 computer running Peak Simple 2 software for system control.

Autosampler vials were equilibrated for 24 minutes at 30°C. An aliquot of gas from the headspace was flushed through the 1.0-mL sample loop, overfilling the loop. The sample was then injected onto the head of the column where the analytes were chromatographically resolved using an

isocratic temperature program at 100°C. The peaks in the chromatogram were integrated and the results were reported as measured peak heights.

Chemicals

Reagent grade trichloroethylene from Fischer Scientific was used to prepare the analytical standards. Analytical grade water was purified by a Milli-Q Type 1 Reagent Grade Water System (Millipore Corporation). HPLC-grade methanol used to prepare the analytical standards was obtained from Sigma-Aldrich.

Preparation of stock standard

A high standard solution was prepared by diluting 0.145 g of TCE to 25 mL with methanol in a volumetric flask, yielding a concentration of 5.80 g/L. A low standard was prepared by diluting 0.0116 g TCE to 25 mL with methanol, resulting in a concentration of 0.464 g/L. The standards were stored at 4°C, with the stoppered joints wrapped with Parafilm to retard evaporation.

Preparation of analytical standards

Analytical standards were prepared by adding 10 mL of reagent grade water to a 22-mL headspace autosampler vial, then capping the vial. The vial was then inverted and an aliquot of the stock standard was injected into the water through the septum via syringe. Different volumes of the stock standards were used to prepare the initial and daily calibration standards for analysis (Table 2).

Table 2. Concentration of initial calibration standards.

Standard	*Stock*	*Volume (mL)*	*Final (mg/L)**
1	high	50	29,000
2	high	30	17,400
3	high	10	5,800
4	low	50	2,320
5	low	30	1,390
6	low	10	464

* Concentration of TCE in the water.

Initial calibration

For the initial calibration, six standards were prepared. Standards 1–3 were prepared by injecting 50, 30, and 10 µL of *high* standard, respectively, into 10 mL of water in a headspace autosampler vial, as described in the previous section. Standards 4–6 were prepared by injecting 50, 30, and 10 µL of *low* standard, respectively, into 10 mL of water as previously described. The concentration of TCE in the standards is listed in Table 2.

Each calibration standard, as well as a blank, was analyzed by gas chromatography with photoionization detection (GC/PID) in duplicate in a random order. The measured peak height was plotted against the concentration of the standard. A linear model was fitted to the data using simple

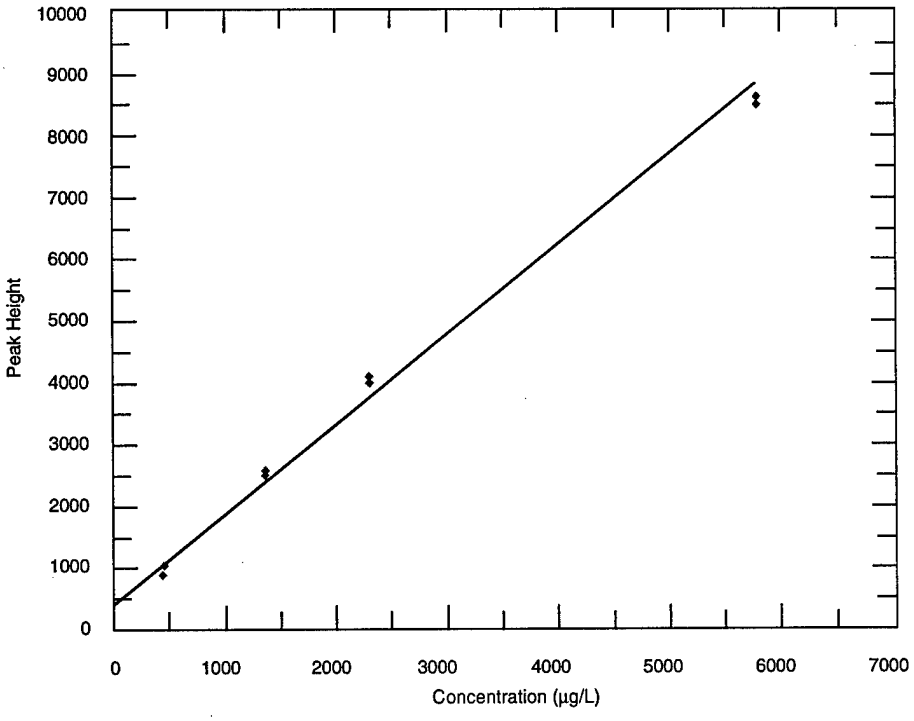


Figure 5. Initial calibration curve for TCE analysis by GC/PID.

linear regression. The data show that the response is linear up to 5800 µg/L (Fig. 5).

Daily calibration

A daily calibration standard was prepared by injecting 20 µL of the *low* stock standard into 10 mL of water as described above. The vial was then shaken vigorously, by hand, for 1 minute to establish the equilibrium headspace concentration. A sufficient number of replicates was prepared such that three standards were analyzed at the start of the analysis, and additional replicates were analyzed after every sixth sample and as the final sample of the analysis. A peak height response for the TCE was recorded for each analysis and the mean peak height response calculated. The daily response factor was calculated by taking the ratio of the mean peak height response over the concentration of the standard. The resulting units for the response factor were peak height per microgram per liter.

Sample collection

We collected water samples in 22-mL headspace autosampler vials. The vials were overfilled with the water sample, then capped with an open top crimp cap and a gray butyl, Teflon-lined septum.

During the loading process, influent and effluent water samples were collected. The influent water was collected before it passed through the packed adsorption bed and the effluent water was collected after. The first hour, samples were collected at time 0, 15, 30, 45, and 60 minutes. For the next 2 hours, samples were collected every 30 minutes, then every hour up to 7 hours. On subsequent days, samples were collected every 2 hours during the work day (four times).

Sample collection continued until the columns were determined to be loaded. The influent samples were collected directly from the holding tank by submerging the vials with the open end pointed upwards. The effluent samples were collected from a sampling port at the top of the columns. When sampling, we closed the drain port to raise the level of the water in the column above the sampling port. This was done to ensure that samples were not being collected at the water/air interface where the concentration could be varying because of volatilization. Upon collection of the samples, the drain port was reopened. During the remediation phase, water samples were collected daily in a way identical to that used for the effluent samples. All water samples were collected in triplicate.

Clay samples were collected on day zero, then every third day, in the morning. Samples were collected from the top of the columns. The cap of the column was removed and a scintillation vial was lowered down to the center of the fluidized bed on the end of a heavy gauge copper wire. The vial was raised slowly through the fluidized bed to allow the maximum amount of clay to be collected. The vial was removed from the wire and immediately capped with an aluminum-faced screw cap. A single clay sample was collected at each sampling event.

Sample preparation

Water samples were prepared for headspace analysis by removing a 12-mL aliquot of water from the vial with a needle and syringe. The needle was inserted into the vial to allow air to be drawn in while the syringe removed water, thus creating a headspace at atmospheric pressure. The vial was then shaken vigorously, by hand, for 1 minute to establish the equilibrium headspace concentration. Note that, during the remediation phase, the 12-mL aliquot removed from the vial was transferred to a scintillation vial and held for subsequent phenol analysis. After the headspace analysis was performed, the sample was held for subsequent chloride analysis.

To analyze the clay samples, a 1-g subsample was removed from the collection vial using a 3-cm^3 modified plastic syringe. The syringe was modified by cutting off the Luer Lok tip and removing the rubber tip from the plunger. In the syringe 1 g of the wet clay material was equivalent to approximately 1.5 cm^3. The subsample was transferred to a second scintillation vial that contained 1.0 mL of methanol. This vial was then capped and placed in an ultrasonic bath for 10 minutes. The methanol was removed and transferred to another vial. A second 1.0-mL aliquot of methanol was added to the clay sample and the sample was again sonicated for 10 minutes. Two additional 10-minute extractions with 1.0 mL of methanol were performed (four extractions in total). The methanol extracts were all combined in one vial. The vial was centrifuged for 2 minutes at 2500 rpm to separate the suspended solids from the liquid. Three 100-µL aliquots of the extract were each transferred via syringe to previously sealed, 22-mL headspace autosampler vials, each containing 10 mL of water. This vial was shaken vigorously by hand for 1 minute to establish the equilibrium headspace concentration.

Sample analysis

All headspace standards and samples were analyzed using the headspace GC system described

above. Each vial was equilibrated at 30°C for 24 minutes. The vial was then pressurized, forcing an aliquot of the headspace into a 1-mL sampling loop. The loop was put in line with the carrier gas, thus transferring the sample to the head of the chromatographic column (Restek MXT-1 megabore [15 m × 0.530 mm i.d.]). The column temperature was maintained at 100°C throughout the entire run. The analytes were detected with a photoionization device operated with a source current of 80 μA. Chromatographic results were reported as peak height measurements.

Calculations

Daily response factors were calculated as described above. The concentration of TCE in the water samples was calculated by dividing the peak height response for the sample by the daily response factor

$$[TCE]_j = (\text{peak height})_j / (\text{response factor}) \quad (1)$$

where (j) denotes each individual sample. This resulted in a concentration value in the units of micrograms per liter in the water sample. Note that, although the direct analysis was of the headspace, the response factor was determined relative to the concentration of the water. This assumes that the partitioning of the TCE between the water and headspace was equivalent for both the standards and the samples; thus, the determination of the concentration of TCE in the headspace can be algebraically factored out.

The concentration of TCE in the clay samples was calculated by determining the concentration in the analyzed sample (j) using eq 1, then, with eq 2, back-calculating to the concentration in the clay using the dilution factor of 100 μL to 10 mL from the transfer of the aliquot of extract to the water in the vial, and the exact weight of the soil sample.

$$[TCE]_{clay}\ (\mu g/g) = [(TCE)_j\ (\mu g/L)/0.81] \cdot (100) \cdot [0.004\ (L)/w(g)] \quad (2)$$

where 0.81 = correction factor
100 = dilution factor
0.004 L = combined volume of extract from the four extractions
w = wet weight of the sample (g).

Analysis for phenol

Instrumentation

All of the analyses for phenol were performed using a high performance liquid chromatographic (HPLC) system composed of the following components:

- A Spectra Physics Model SP8810 precision isocratic pump.
- A Spectra Physics Model Spectra 100 variable wavelength UV detector set at 254 nm.
- A Dynatech LC-241 precision autosampler equipped with a Rheodyne Model 7010A sample loop injector and a 100-μL loop.
- An Alltech Model 3000 solvent recycling system.
- A Hewlett Packard Model HP3396 digital integrator equipped with a Hewlett Packard Model HP9114B disk drive.

The autosampler was used to introduce samples by flushing the 100-μL loop for 20 seconds at a rate of 0.5 mL/min. The phenol was separated on an LC-18 (25 cm × 4.6 mm i.d., 5 μm) reversed-phase column (Supelco, Inc.) eluted with a binary eluent of water and methanol (1:1, v/v) at a flow rate of 1.4 mL/min. Chromatographic results were reported as peak height measurements.

Chemicals

The phenol used to prepare the analytical standards was from Sigma-Aldrich. The analytical grade water in which the standards were prepared was purified by a Milli-Q Type 1 Reagent Grade Water System (Millipore Corporation). Methanol used for the chromatographic eluent was from J.T. Baker.

Preparation of stock standard

A stock standard of phenol was prepared by dissolving 50 mg of phenol in reagent grade water and diluting to 100 mL in a volumetric flask. The resulting concentration was 500 mg/L.

Initial calibration

For the initial calibration for the phenol analysis, a series of standards was prepared as a dilution of the stock standard. Table 3 lists the details of the dilutions and the concentration of phenol in the calibration solutions.

Table 3. Preparation and concentrations of calibration solutions.

Calibration solution	*Dilution from stock standard*	*Concentration (mg/L)*
Stock standard		525.0
Solution 1	10:25	210.0
Solution 2	5:25	105.0
Solution 3	1:25	21.0

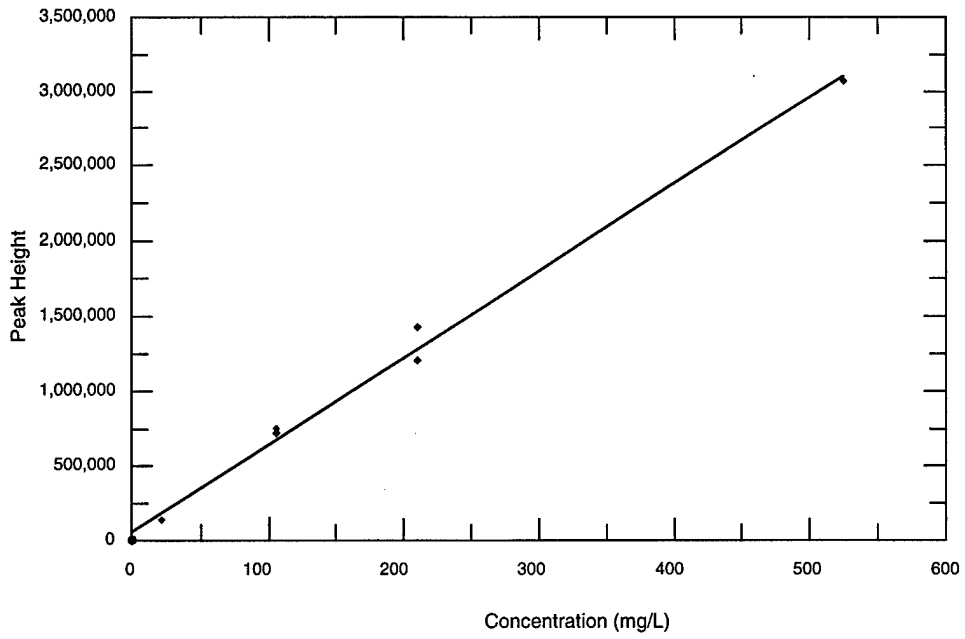


Figure 6. Initial calibration curve for the analysis of phenol by HPLC-UV.

All dilutions were made using reagent grade water in 25-mL volumetric flasks. The stock standard and each calibration solution were analyzed in duplicate. The integrated peak area was plotted against the concentration of the solutions. A model was fitted to the data using linear regression. The data show that the response is linear up to 525 mg/L (Fig. 6).

Daily calibration

An analytical standard was prepared by dissolving 35 mg of phenol in reagent grade water and diluting to 100 mL in a volumetric flask. The resulting concentration was 350 mg/L. This standard was used throughout the project for daily calibration. Each day of analysis, three aliquots of the standard were analyzed, two at the start and one at the end of the analysis. A peak area response for the phenol was recorded for each replicate and the mean peak area response was calculated. The daily response factor was calculated by taking the ratio of the mean peak area response over the concentration of the standard. The resulting units for the response factor are peak height per milligram per liter.

Sample collection

Two samples from each column were collected daily for phenol analysis during the remediation phase of the test. These samples consisted of the 12-mL aliquots that were removed from each vial when the samples were prepared for headspace analysis. Refer to the *Sample Collection* and *Sample Preparation* sections of the TCE analysis for details.

Sample preparation

Samples for phenol were prepared for analysis by passing them through a Millex-HV (0.45-µm) disposable filter. Aliquots of the filtered samples were transferred to HPLC autosampler vials using Pasteur pipettes.

Sample analysis

All phenol standards and samples were analyzed using the HPLC system described above. The autosampler was programmed to flush the sampling loop for 20 seconds at a rate of 0.5 mL/min. The samples were then injected onto an LC-18 column eluted with 1:1 (v/v) water/methanol. Detection was performed with a UV detector set at 254 nm. The chromatogram was recorded by the Hewlett Packard digital integrator programmed to integrate peak areas.

Calculations

Daily response factor was calculated as described above. The concentration of phenol in the water samples was calculated by dividing the peak height response for the sample by the daily response factor

$$[\text{phenol}]_j = (\text{peak height})_j / (\text{response factor}) \quad (3)$$

where (j) denotes the analyzed sample. This resulted in a concentration value in the units of milligrams per liter in the water sample.

RESULTS AND DISCUSSION

Loading

Skid 1 was initially loaded at a flow rate of 240 mL/min, and the first effluent samples were collected after 2 hours. The data showed that the effluent concentration was already 40% of the influent and had risen to near 60% after 4 hours of loading (Fig. 7).

This suggested that the loading curve had a very sharp rise in the first hour. Data also suggested that the contact time between the groundwater and the clay sorbent was too short to retain sufficient TCE. As a result, the flow rate was reduced to 120 mL/min and samples were collected every 15 minutes for the first hour. In addition, we decided that distilled water would be used while setting the loading flow rates. The time required to set the flow accurately was nearly 30 minutes. If the contaminated groundwater had been used during this time, then loading of the columns would have been started, confounding the description of the loading curve.

The data from the five subsequent loadings show that the loading curve indeed has a very sharp rise in the first few hours, then starts to level off after about 6 hours. Figure 8 is representative of

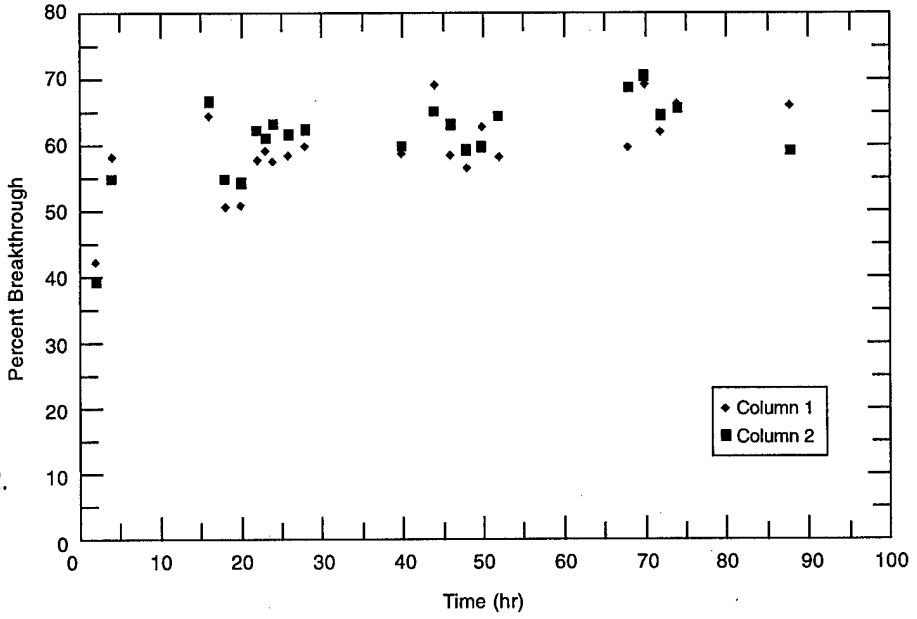


Figure 7. Initial loading curves for columns 1 and 2.

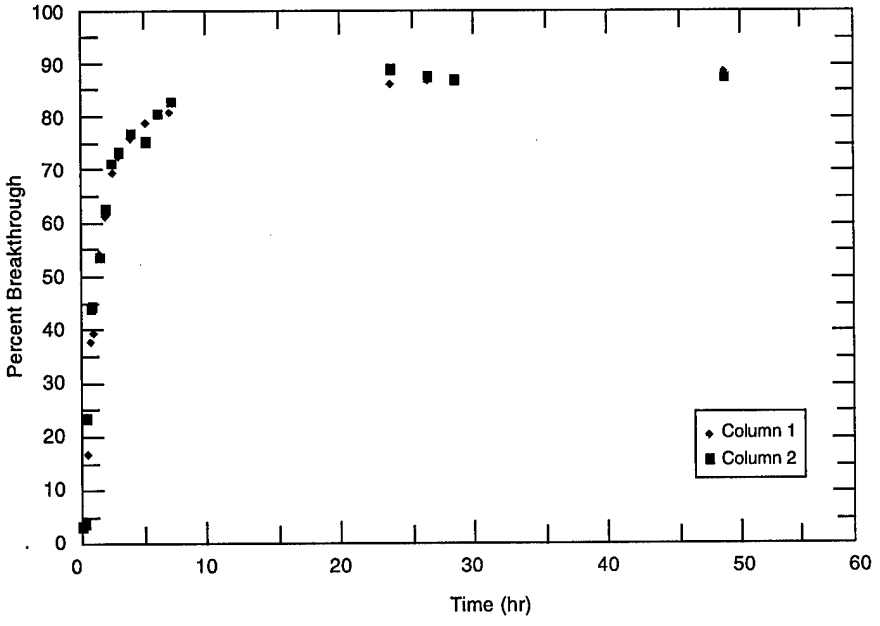


Figure 8. Third loading curve for columns 1 and 2.

Table 4. Results of loading process.

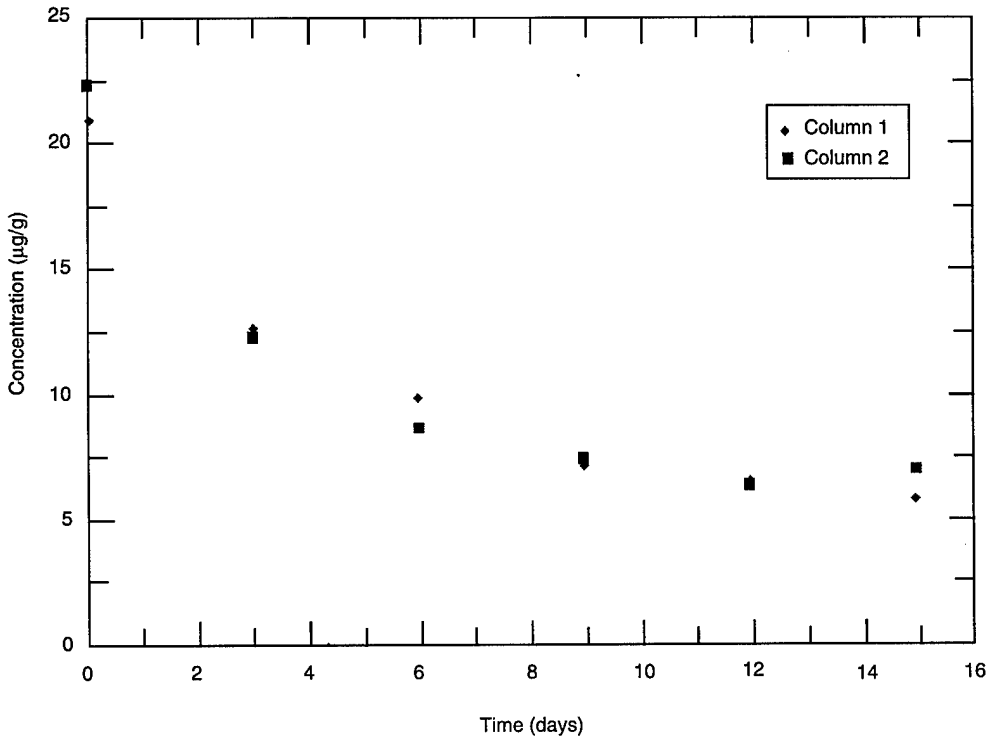
Round	Column	Loading time (hr)	TCE concentration in clay (µg/g)
1	1	88	43.5
	2	88	57.1
	3	74	32.4
	4	74	36.6
2	1	140	21.0
	2	140	22.2
	3	54	30.9
	4	54	23.5
3	1	50	32.2
	2	50	33.6
	3	48	28.6
	4	48	26.9

all of the loading curves. The first three loadings were run for 88, 74, and 140 hours, respectively. The other three were run for approximately 50 hours each. The average amount of time required to achieve the "loaded" mark was approximately 36 hours.

To evaluate the reproducibility of the loading process, we examined the initial TCE concentration of the clay sorbent prior to starting the remediation phase. Results of the loading process are presented in Table 4. The average concentration was found to be 32.4 µg/g, with a relative standard deviation of 31% and a range from 21.0 to 57.1 µg/g. The data show that, with the exception of columns 1 and 2 for round 1 and columns 1 and 2 for round 2, the TCE concentration in the clay sorbent was very reproducible. The average concentration, excluding these runs, which resulted in extreme values, was 31.0 µg/g, with a relative standard deviation of 13%. The low concentration found for columns 1 and 2 in round 2 was attributed a long holding time (10 days) between the loading of the columns and the remediation of the sorbent. No suitable explanation could be attributed to the high concentrations found for round 1, columns 1 and 2.

Bioremediation of sorbent

During the remediation phase, water samples were collected and analyzed daily for TCE, phenol, and chloride. Clay samples were collected and analyzed for TCE every third day. Although the concentration of TCE was monitored in both the water and the clay during the remediation process, the system's performance was primarily evaluated on the basis of the clay data because our objective was to rejuvenate the clay for reuse. The TCE in the



a. Concentration vs. time.

Figure 9. Remediation curves for TCE in clay for round 2, columns 1 and 2.

water was determined daily, primarily to ensure that the system was operating properly. The concentration of phenol was monitored because the microbiological system required that a minimum concentration of phenol be maintained in the reactors for the process to continue. The chloride concentration was monitored to demonstrate the mineralization of the TCE and for mass balancing.

The clay data were examined in two ways: absolute concentration vs. time (Fig. 9a) and relative concentration vs. time (Fig. 9b). The data are summarized in Table 5. The concentration data for the TCE in water were also plotted vs. time (Fig. 10).

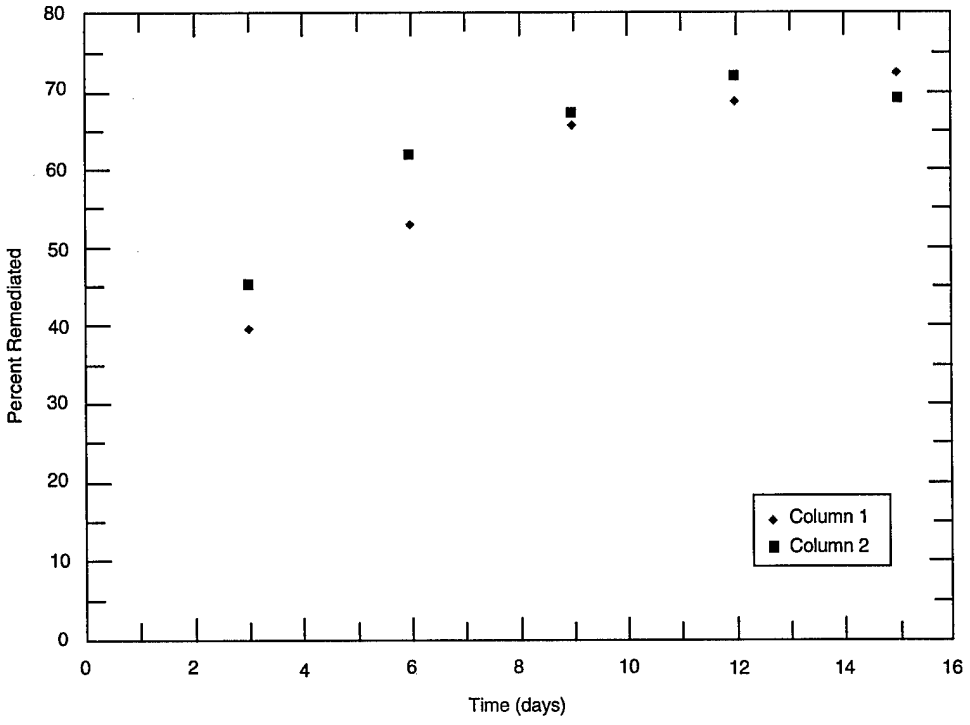
The data show that the average absolute concentration of TCE in the clay was reduced by 26.3 µg/g across all the rounds of the study. This amounts to an average percentage reduction of TCE in the clay of 78.2%, with a relative standard deviation of 16%. These data suggest that the adsorbent material can be remediated and that the process was reproducible. The average time required for the remediation phase was 13 days.

A comparison of the concentration data vs. time for the clay and water samples suggested that the remediation process was desorption limited. The microbiological process takes place in the water, not on the surface of the clay, and the concentration in the water drops at a faster rate than that in the clay during the first few days of the remediation process. If the remediation were limited by the microbiological process, we would see the concentration in the water remain relatively constant as long as there was TCE desorbing from the clay.

In addition to a desorption limitation, the data also suggested a mass limitation. Each of the col-

Table 5. Summary of clay remediation data.

Round	*Column*	*Starting conc. (µg/g)*	*Ending conc. (µg/g)*	*Percent remediated*	*Number of days*
1	1	43.5	< d	99.9	15
	2	57.1	< d	99.9	15
	3	32.4	8.29	74.4	15
	4	36.6	8.56	76.6	15
2	1	21.0	5.81	72.3	15
	2	22.2	6.91	68.9	15
	3	30.9	6.20	80.1	12
	4	23.5	10.8	54.2	12
3	1	32.2	6.20	80.8	12
	2	33.6	8.50	74.7	12
	3	28.6	5.47	80.9	9
	4	26.9	6.63	75.3	9
mean		32.4	6.11	78.2	13
std. dev.		10.1	3.23	12.4	



b. Percentage remediated vs. time.

Figure 9 (cont'd).

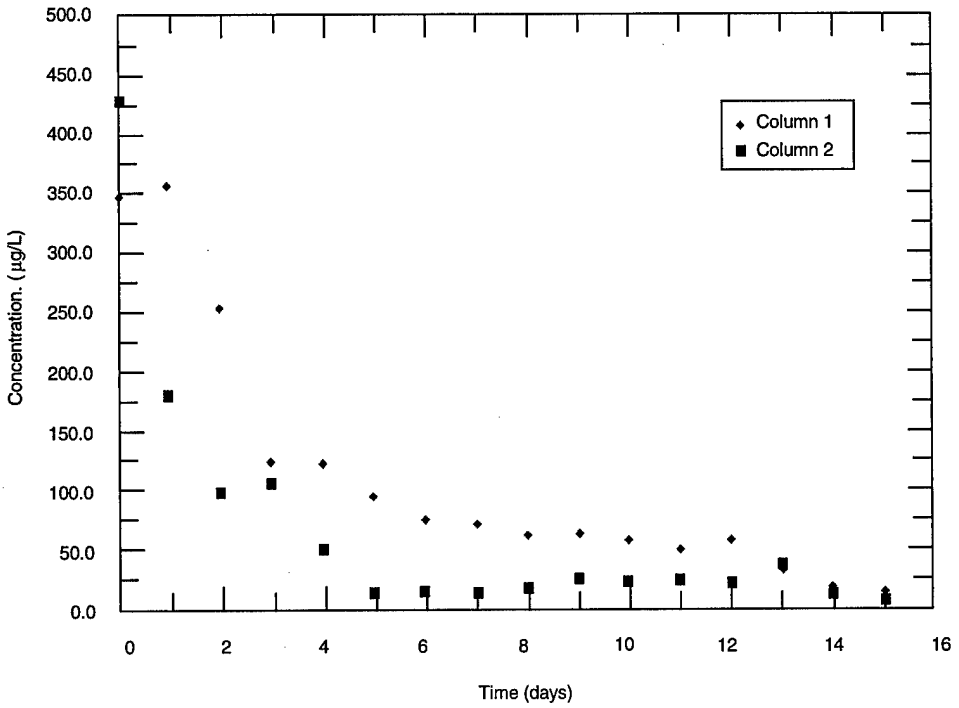


Figure 10. Remediation curve for TCE in water for round 2, columns 1 and 2.

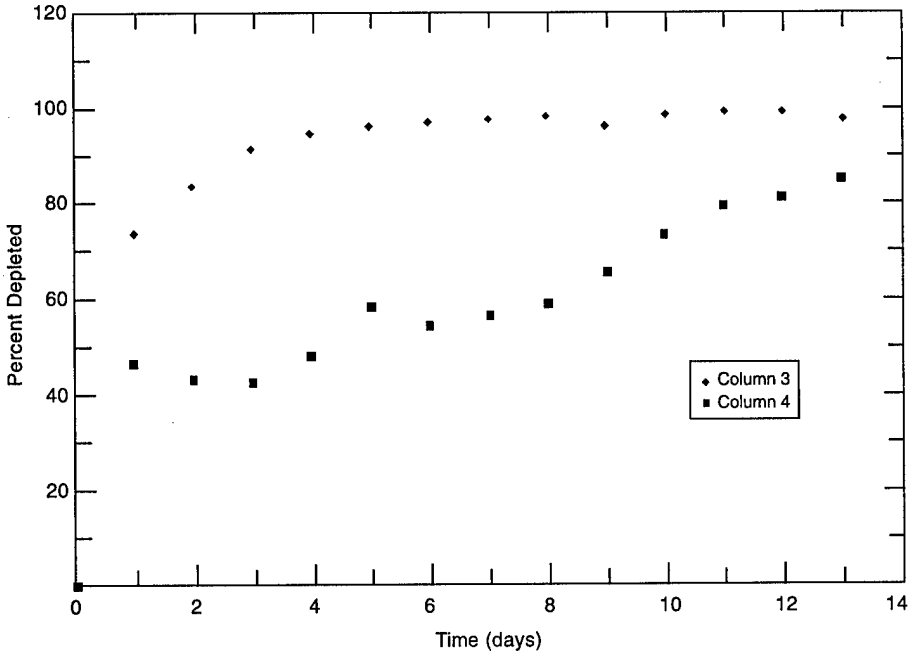


Figure 11. Remediation curve for TCE in water for round 2, columns 3 and 4.

umns had 2200 g of adsorbent material. Based on the average concentration change for each remediation cycle, the mass of TCE actually removed from the system was only 58 mg per column.

During the course of this pilot study, we observed two factors that seemed to have a direct effect on the remediation rate. The first was the removal of the carbon dioxide. During the remediation of columns 3 and 4 of round 2, the concentration of TCE in column 4 was not being reduced significantly (Fig. 11). Additional biomass was added, but the remediation process remained slow, although laboratory testing of a water sample from columns 3 and 4 confirmed the presence of viable G4 microorganism. When the bioreactors were being set up for the next remediation, a fail-

ure in the line used to draw carbon dioxide from the reactors was discovered. At first, this was not considered the cause of the stunted remediation, but, in a later round, we observed again a slowing of the TCE reduction in the water early on during the cycle. Again, a leak was found in the same section of tubing. The leak was repaired and the subsequent data showed that the process resumed its normal rate.

The second factor that seemed to have a direct effect on the rate of remediation was the maintenance of the phenol concentration. The bench-top results indicated that the process would continue with a phenol concentration as low as 60 mg/L. We observed, though, that when the concentration of the phenol dropped to that level during the first few days of the remediation, the microbiological process seemed to slow down. For the later rounds, we maintained the phenol concentration near 300 mg/L for the first few days and we found that the total time required for the remediation step was shortened.

We were also able to make some observations on the effect of temperature on the remediation. The skids were originally set up outside, with a wood and plastic shell around them. The temperature inside the structure would vary dramatically, from less than 0 to 20°C ambient air temperature in the mornings to near 40°C in the afternoons when the sun was directly shining on the structure. Owing to the time of year and the drop of daily temperature to below freezing, the skids were moved into a building where the temperature was maintained at approximately 4.5 to 7°C. The data from the remediations carried out at the lower temperature do not indicate that the rate of the process was being affected by this.

The concentration of chloride in the water was monitored throughout the pilot study for mass balancing and to demonstrate the mineralization of the TCE. Based on the mass of TCE being processed, the expected change in the chloride concentration was approximately 2.6 mg/L. The background chloride concentration of the groundwater was approximately 15 ± 3 mg/L. Thus, we were unable to measure the small concentration change that results from the mineralization of the TCE. Subsequently, we were unable to perform a mass balance on the remediation process.

CONCLUSION

The data from this pilot study showed that the packed adsorbent bed could be loaded in approximately 36 hours at a flow rate of 120 mL/min. The concentration of TCE in the clay at the end of each loading cycle indicated that the loading process was reproducible. The remediation phase of the process took approximately 13 days. The reduction in the TCE concentration in the clay during each round of the study told us that the sorbent was being remediated by the microbiological process. The combination of this information illustrated that the adsorbent material could be repeatedly loaded and remediated, thus meeting the objective of its rejuvenation. Areas that need to be improved are the rate of remediation and the loading capacity of the adsorption beds. Currently, each complete cycle of loading and remediating requires 2 weeks while only mineralizing 58 mg of TCE per column.

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Volatile organic compounds (VOCs) are a major source of water contamination in the U.S. They pose a threat to the environment and are a potential hazard to human health. Trichloroethylene (TCE) is the most common of these pollutants. TCE is usually remediated through pumping and treating it, using either air stripping or granular activated carbon. Bioremediation is an alternative treatment that uses microbes to convert hazardous substances into nonhazardous compounds. A fluidized bed adsorption bioreactor is examined here for the treatment of groundwater contaminated at low concentrations. This pilot study showed that the packed adsorbent bed could be loaded in approximately 36 hours at a flow rate of 120 mL/min. The remediation phase of the process took approximately 13 days. The reduction in the TCE concentration in the sorbent during each round indicated that it was being remediated by the microbiological process. Areas that need to be improved are the rate of remediation and the loading capacity of the adsorption beds. Currently, each complete cycle of loading and remediating requires 2 weeks while only mineralizing 58 mg of TCE per column.

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