CASE STUDY OF EX-SITU BIOLOGICAL TREATMENT OF PERCHLORATE-CONTAMINATED GROUNDWATER

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ABSTRACT

Groundwater in certain areas at Longhorn Army Ammunition Plant (LHAAP) (Texas) contains volatile organic compounds (VOCs) and perchlorate from past operations at the site. Groundwater from a Burning Ground and Landfill is currently being remediated by pumping the water from an interceptor collection trench system to the surface, removing VOCs and metals in an *ex-situ* treatment process, and discharging the treated water to a nearby stream. In early 2000, LHAAP's environmental restoration team took steps to supplement the existing treatment process with a biological fluid bed reactor (FBR) to remove the perchlorate prior to surface water discharge. After preliminary FBR sizing and costing information were obtained, a laboratory treatability program was undertaken to confirm the system design assumptions and demonstrate the effectiveness of the FBR process for treating the LHAAP groundwater. Approximately 650 gallons (2,460 liters) of LHAAP groundwater containing 11,000 to 23,000 (average 16,500) µg/L of perchlorate were used for the evaluation. Both acetic acid and ethanol were investigated as growth (i.e. electron donor) substrates. For the majority of the test, effluent perchlorate concentrations were below the quantitation limit of 5 µg/L, except when the laboratory FBR was operated at a low substrate load to determine the point of treatment failure. The target effluent perchlorate concentration was 350 µg/L. Based on the success of the laboratory test, a full-scale FBR system with the capacity to treat 50 gallons per minute (gpm) (190 liters per minute) of LHAAP water has been installed at the groundwater treatment plant. System start-up occurred in February 2001. The system quickly achieved the target level of perchlorate removal within three weeks of start-up, and has routinely removed perchlorate to less than the limit of detection during normal operation.

1. BACKGROUND

Groundwater in certain areas at Longhorn Army Ammunition Plant (LHAAP) contains volatile organic compounds (VOCs) and perchlorate from past operations at the site. Groundwater from a Burning Ground and Landfill is currently being remediated by pumping the water from an interceptor collection trench system to the surface, removing VOCs and metals in an *ex-situ* treatment process, and discharging the treated water to a nearby stream. In early 2000, LHAAP's environmental restoration team took steps to supplement the existing treatment process to remove the perchlorate prior to surface water discharge. After a review of existing treatment options, the LHAAP environmental restoration team chose a biological fluid bed reactor (FBR) (supplied by the team of Envirogen and USFilter/Envirex Products) to remove the perchlorate based on the FBR's proven field effectiveness (Greene and Pitre, 2000; Hatzinger et al., 2000; Sutton and Greene, 1999). Prior to installing the FBR, a laboratory study was conducted to confirm the system design assumptions and show the effectiveness of the FBR process for treating the LHAAP groundwater. Based on the success of the laboratory test, a full-scale FBR system with the capacity to treat 50 gallons per minute (gpm) (190 liters per minute) of LHAAP water was installed at the groundwater treatment plant. System start-up occurred in February 2001. This paper describes the FBR process for treatment of perchlorate, summarizes the results of the laboratory pilot study, describes the full-scale FBR system installed at LHAAP, and presents the full-scale perchlorate removal data to date.

2. THE FBR PROCESS

The effectiveness of a biological system is dependent on maintaining a highly active biomass concentration in the bioreactor. Fixed-film bioreactors cultivate organisms that prefer to grow attached to surfaces. FBRs are highly efficient fixed-film bioreactors that rely on the immobilization of microbes on a hydraulically fluidized bed of media particles (Figure 1). These particles provide an extremely large surface area for growth of biological films, thus producing a large amount of biomass in a small reactor volume. The bed of particles is fluidized to reduce back-pressure resistance to flow by directing reactor influent passes through a distribution system at the bottom of the bed that establishes a uniform upflow velocity distribution within the fluidized bed. The fluidization rate is constant and set at a rate that causes a 25 to 30 percent expansion of the bed. As biological films grow on the particles, making them less dense, the bed further expands. Feed flow and recycle flow are blended to provide the necessary up-flow velocity for fluidization. The choice of media depends on the nature and concentration of the target compounds to be treated. Sand is sometimes chosen for treatment of water containing high concentrations of organics, where the inventory of biomass in the FBR is expected to be large (i.e., high biofilm growth applications). Granular activated carbon (GAC) is often selected when the treatment criteria is very stringent [i.e., treatment down to µg/L levels]. If needed, oxygen is supplied by a bubbleless aeration device (shown in Figure 1).

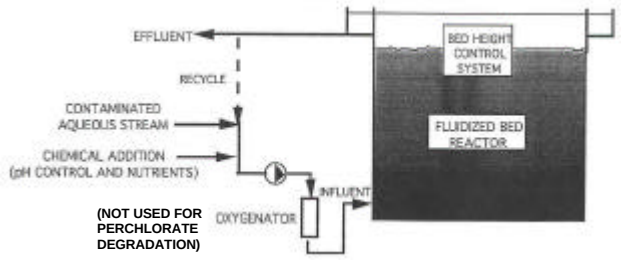

Figure 1. General FBR system process schematic

For treatment of perchlorate (and nitrate), oxygen is not added to the reactor. Instead, perchlorate (and/or nitrate) functions as the terminal electron acceptor, and an appropriate electron donor (typically an organic substrate) is added to the reactor in an amount sufficient to consume all the perchlorate (and residual oxygen and nitrate) present. Several microbial strains have been identified with the ability to degrade perchlorate by using the molecule as a terminal electron acceptor during growth on either an inorganic or organic substrate. The enzymatic pathways involved in perchlorate reduction have yet to be fully elucidated. However, a perchlorate reductase enzyme appears to catalyze an initial two-step reduction of perchlorate (ClO_4^-) to chlorate (ClO_3^-) and then chlorite (ClO_2^-). The chlorite is further reduced by a chlorite dismutase enzyme to chloride (Cl^-) and oxygen (O_2). Thus, the microbial degradation of perchlorate produces two innocuous products, chloride and oxygen.

3. LHAAP FBR TREATABILITY STUDY

3.1 Overview

The laboratory FBR treatability program was designed to generate process data for use in designing and assessing the performance of a full-scale FBR to treat the LHAAP groundwater. Operating parameters were evaluated using two different electron donors (carbon sources). The program consisted of four phases:

Phase 1: Sample characterization;
Phase 2: Start-up and acclimation of biomass;
Phase 3: Steady operation of the laboratory FBR system;
Phase 4: Data interpretation and report generation.

3.2 Laboratory System Description

The laboratory FBR system was constructed of glass, stainless steel, and Teflon® materials to minimize abiotic chemical losses. The system had a total liquid volume hold-up of approximately 4 liters with an empty bed volume of approximately 1,000 mL. Figure 2 is a process flow schematic of the laboratory FBR system.

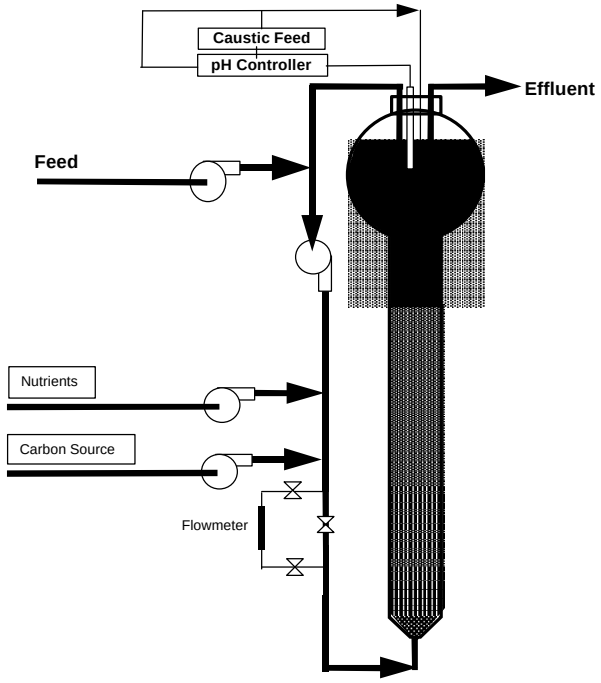

Figure 2. Laboratory FBR flow schematic

Groundwater samples from LHAAP were shipped to Envirogen in 55-gallon (200-liter) drums for processing through the laboratory FBR. The drums were kept in a cool environment prior to use. The groundwater feed to the FBR was introduced in the recycle line on the downstream side of the recycle pump. Based on the concentrations of perchlorate present, GAC was chosen as the biofilm support media for this application. Both acetic acid and ethanol were investigated as electron donor substrates for the LHAAP groundwater. These carbon sources were added with a syringe pump into the combined feed and recycle flow (i.e. influent flow) of the FBR at doses equal to or greater than the minimum theoretical amounts [i.e. minimum total organic carbon (TOC) requirements] needed to reduce all the perchlorate, chlorate, nitrate, and oxygen present in the feed, as well as support growth of biomass. The equations used to determine these amounts are similar to those used for nitrate reduction (i.e., denitrification) reactions (USEPA, 1993). The GAC bed in the reactor was initially charged to give a settled bed volume of approximately 800 mL, and was fluidized to approximately 1,000 mL using a peristaltic pump on the recycle line. The reactor pH was controlled by direct addition of caustic. A portion of the liquid that overflowed the top of the reactor was recycled to maintain fluidization; the balance exited as treated effluent.

The laboratory FBR system operated 24 hours a day, 7 days a week. The pre-acclimation of biomass (Phase 2) was accomplished by pumping a synthetic feed containing approximately 25,000 µg/L of perchlorate through the FBR. Pre-growth of biomass compresses the time required to attain steady-state conditions, thereby shortening the overall length of the test program. Groundwater was fed to the laboratory FBR during Phase 3 such that the hydraulic retention time (HRT) through the laboratory unit was the same as that which would occur if 50 gpm (190 L/min) were processed through a standard 5-ft (1.5-m) diameter full-scale FBR (i.e., standard EFB-5.0 design). Key process variables were routinely monitored and/or controlled, including pH, nutrient concentrations, perchlorate concentrations, and soluble TOC concentrations. Soluble nutrients [ammonia-nitrogen (NH_3-N) and ortho-phosphate-phosphorus (PO_4-P)] were continually added to the liquid in the recirculation line using a peristaltic pump to maintain residual NH_3-N and PO_4-P levels greater than 2 mg/L in the effluent. The pH of the reactor contents was automatically controlled through the addition of sodium hydroxide (NaOH). Influent and effluent grab samples were collected periodically for analysis of perchlorate and other compounds (see below). The quantitation limit for perchlorate was 5 µg/L. The temperature of the reactor was maintained at ambient conditions (70-75°F or 21-24°C).

3.3 Sampling and Analytical Methods

The initial wastewater characterization during Phase 1 was performed on a representative sample of the material received. The analytical methods used are outlined in Table 1. These same methods were used during the operation of the FBR in Phase 3. Additional analyses for chloride and sulfide were conducted in Phase 3 using EPA Methods 300.0 and 376.1, respectively. A standard toxicity screening assay was also conducted during Phase 1 to determine if anything inhibitory or toxic to microbial growth was present in the LHAAP groundwater; from the results of this assay, it was determined that nothing toxic was present.

During the operation of the laboratory FBR system, a log was maintained to record flowrates, temperatures, pH, dissolved oxygen (DO) readings, oxidation/reduction potential (ORP), and other pertinent operating data. Influent and effluent grab samples were collected as needed to assess the performance of the system.

3.4 Results and Conclusions

Twelve 55-gallon (200-liter) drums of treated groundwater from LHAAP arrived on 22 May 2000. These samples were collected after the LGAC unit at the LHAAP Groundwater Treatment Plant (following air stripping and metals precipitation also). The contents of three drums were analyzed for DO, perchlorate, chlorate, nitrate-nitrogen, and other components. The results are shown in Table 1. The groundwater samples contained an average of 3.8 mg/L of DO, 14.7 mg/L of perchlorate, 0.5 mg/L of chlorate, and 1.9 mg/L of nitrate-nitrogen. The samples contained minimal amounts of metals, suspended solids, organics, ortho-phosphate, and ammonia-nitrogen. Sulfate concentrations were approximately 300 mg/L.

The LHAAP groundwater began being processed through the laboratory FBR on 13 June 2000 following the Phase 2 start-up period. The flowrate of groundwater through the FBR was generally maintained at the flow needed to duplicate the hydraulic retention time (HRT) through a standard 5-ft diamater full-scale FBR (EFB-5.0) treating 50 gpm (190 L/min). For the first 3.5 weeks of testing, ethanol was used as the electron donor carbon source, and was added to the FBR at a rate that was higher than the theoretical requirement for complete reduction of all the perchlorate, chlorate, nitrate, and oxygen in the feed (including the amount of ethanol required for biomass growth). For the following 1.5 weeks of testing, the ethanol addition rate was reduced to the minimum theoretical requirement. For the final 3 weeks of testing, the electron donor carbon source was changed to acetic acid, and was fed at approximately the same excess TOC level as the initial feedrate of ethanol.

The treatability program ran smoothly, except for three periods when the groundwater feed supply to the FBR was interrupted due to problems with the feed pump. These events are shown in Figure 3, which summarizes the influent and effluent perchlorate data during the test.

Table 1. Initial Characterization of Water from LHAAP Groundwater Treatment Plant

Parameter	Method	Units	Average	Std. Dev.
Oxygen	D.O. Probe	mg/L	3.8	0.4
Perchlorate	EPA 314.0	mg/L	14.7	0.4
Chlorate	EPA 300.0	mg/L	0.5	0.0
Nitrate-N	EPA 300.0	mg/L	1.9	0.1
Nitrite-N	HACH Method 8507	mg/L	0.013	0.003
Ortho-phosphate-P	EPA 300.0	mg/L	<0.2	Not Applicable
Ammonia-N	EPA 350.2	mg/L	<0.5	Not Applicable
Sulfate	EPA 300.0	mg/L	303	11.5
Chemical Oxygen Demand	EPA 410.4	mg/L	30	23.2
Total Organic Carbon	EPA 415.1	mg/L	<1	Not Applicable
Oil & Grease	EPA 413.1	mg/L	Less than 10 mg/L for a composite sample	Not Applicable
Total Suspended Solids	EPA 160.2	mg/L	10	5.3
Volatile Organic Contaminants	SW-846 8260	mg/L	Less than 0.10 to 0.05 mg/L for all on 8260 list except for acetone @ 0.18 mg/L (one of two samples)	Not Applicable
Priority Pollutant Metals	EPA 200.7 and EPA 245.1 (Hg)	ug/L	Less than PQL for all on 200.7 list (and Hg) except for Ni @ 1.8 ug/L and Zn @ 165 ug/L	0.1 for Ni and 47.4 for Zn
Broth Tube Toxicity/Inhibition Test	Internal SOP	N/A	Not Toxic or Inhibitory	Not Applicable

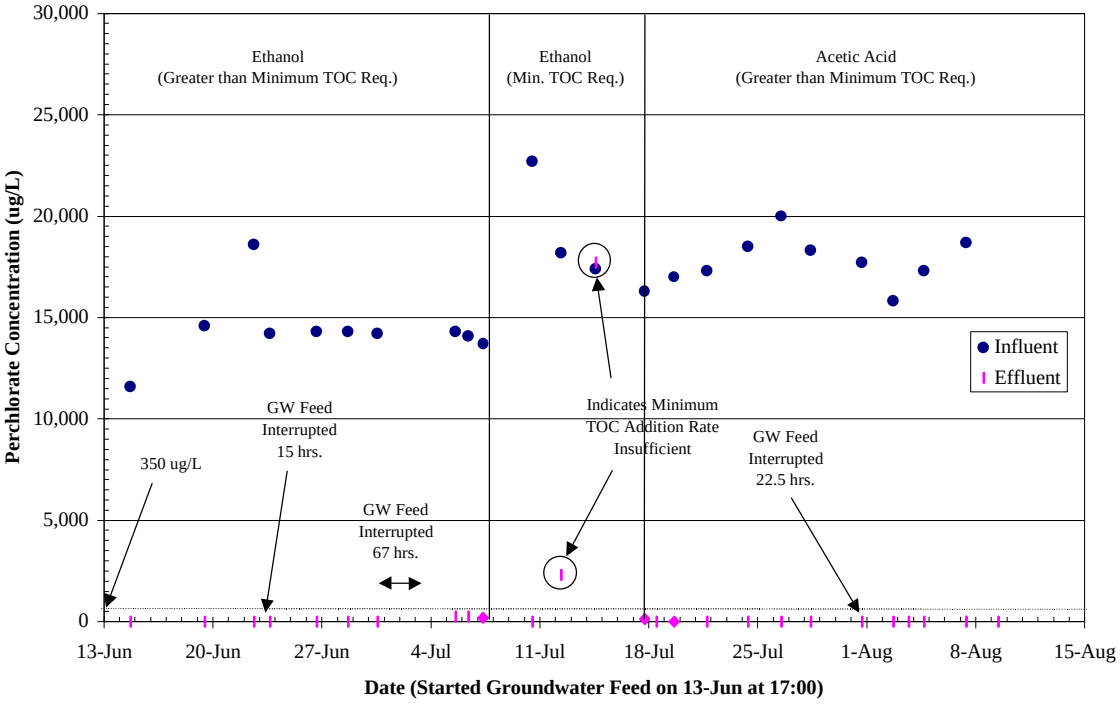

Figure 3. Performance of laboratory FBR

An effluent perchlorate concentration of less than 350 µg/L (the target perchlorate level for LHAAP) was maintained throughout the project using either ethanol or acetic acid as the carbon substrate, except when the laboratory FBR was operated at the minimum theoretical TOC requirement. For the majority of the experiment, effluent perchlorate concentrations were below the quantitation limit of 5 µg/L. In summary, the data showed that a 5-ft (1.5-m) diameter Envirogen/USFilter Envirex Products FBR designed with a standard expanded bed height or greater will achieve the desired perchlorate effluent quality when treating 50 gpm (190 L/min) of LHAAP groundwater (after air stripping and metals precipitation).

4.0 LHAAP FULL-SCALE FBR SYSTEM

4.1 FBR System Description

Based on the success of the laboratory test, a full-scale FBR system with the capacity to treat 50 gpm (190 L/min) of LHAAP water has been installed at the groundwater treatment plant. System start-up occurred in February 2001. The electron donor carbon source for the reactor was chosen to be 50% acetic acid.

The FBR system at LHAAP is composed of a Fluidized Bed Reactor Vessel and an FBR Equipment Skid (see Figure 4). The reactor vessel is 5 ft (1.5 m) in diameter and 21 ft (6.4 m) tall. The influent to the FBR (i.e., the combined feed and recycle) is distributed through a proprietary distribution header at the bottom of the tank. This header is designed to distribute flow evenly and smoothly across the cross-sectional area of the reactor with a minimum amount of turbulence.

To remove excess biomass, there are two patented biomass separation systems at the top of the bed and a third (patent pending) in-bed media cleaning system which can be positioned anywhere along the bed vertically. These devices function to remove excess biomass from the surface of the carbon particles, preventing them from being carried out of the reactor. When biological growth occurs on the fluid bed media, the diameter of the media increases and its effective density is reduced, resulting in an expansion of the media bed beyond that due to fluidization of the bare carbon media. The excess biomass that is separated from the media exits the system through the effluent collection system. Stray carbon particles that exit in the reactor effluent are collected in a Media Capture Tank, and can be periodically pumped back to the reactor.

Feed water is drawn from an equalization tank and combined with recycled water from the FBR vessel at the suction of the influent pump(s). Acetic acid and inorganic nutrients are metered into the water after the influent pump(s) at a rate proportional to the feed water supply to the system. The feed water leaves the FBR Equipment Skid and is piped to the FBR vessel. The treated water at the top of the reactor flows into a submerged recycle collector pipe and an effluent collector pipe under gravity. A portion of the fluid exits the system (i.e., the same volume as the feed to the system), while the balance is recycled back to the FBR vessel influent through the FBR Equipment Skid.

Figure 4. Full-scale FBR system at LHAAP during construction

4.2 FBR System Operation

On February 16, 2001, the FBR was inoculated with approximately 10 cubic feet of pre-conditioned GAC containing biosolids acclimated to perchlorate removal. Within three weeks of inoculation, the system was achieving its treatment objective of <350 µg/L of perchlorate in the effluent. The groundwater flow to the FBR has varied from 20 to 50 gpm (75 to 190 L/min) over the first 110 days of operation, averaging 30 to 35 gpm (115 to 130 L/min). Figure 5 shows the perchlorate removal of the system over the first 110 days. During normal operation, the FBR system has routinely removed perchlorate to less than the limit of detection.

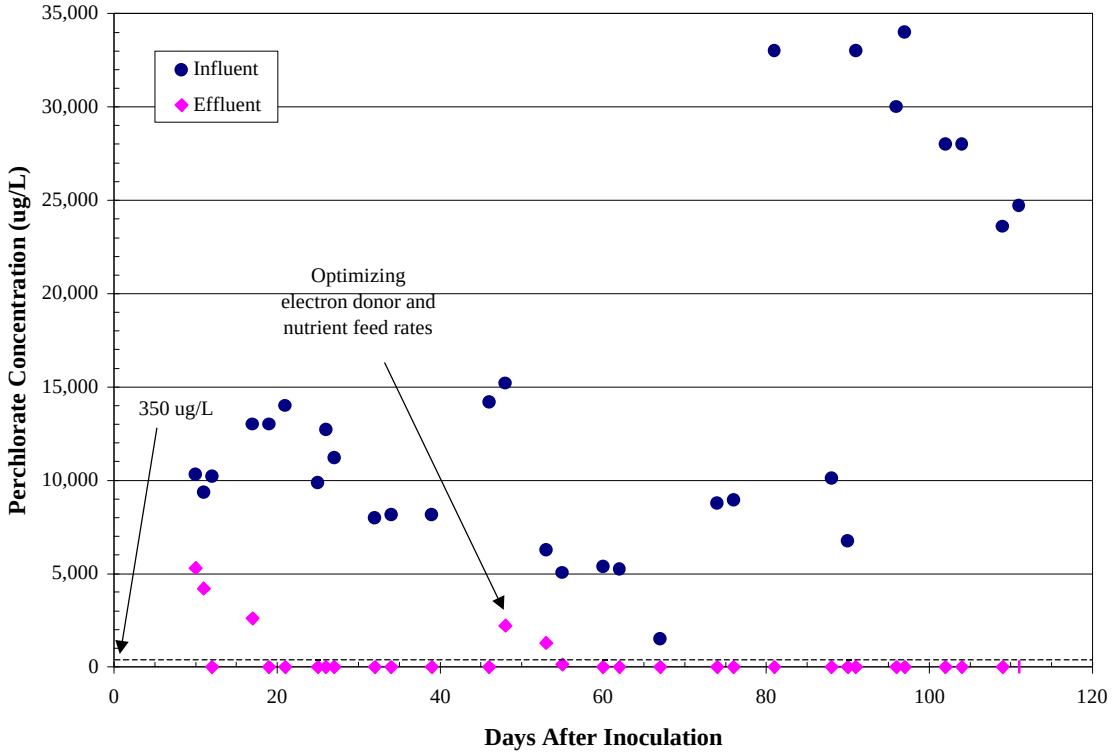

Figure 5. Performance of full-scale FBR at LHAAP

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