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BIOLOGICAL TREATMENT OF PERCHLORATE-CONTAMINATED GROUNDWATER USING FLUIDIZED BED REACTORS

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ABSTRACT: A laboratory pilot study was conducted using fluidized bed reactors (FBRs) to treat groundwater containing ammonium perchlorate. The pilot bioreactors consisted of glass columns containing fluidization media and equipped with automatic pH control, variable speed feed, influent and effluent pumps, water feed and collection tanks, and systems for the addition of substrates and nutrients for bacterial growth. The treatment of site groundwater containing a high concentration of perchlorate (400 mg/L) as well as chlorate (480 mg/L) and nitrate (20 mg/L) was evaluated. Sand-based FBRs fed ethanol as an electron donor reduced all three chemicals below quantitation limits. A full-scale FBR system designed to treat up to 4,000 gal/min of groundwater with perchlorate is currently in operation in California. This system, which consists of four FBRs, has been treating groundwater with perchlorate concentrations ranging from 6 to 8 mg/L. Perchlorate in effluent water has been below the practical quantitation limit (< 0.004 mg/L) during its operation.

INTRODUCTION

Ammonium perchlorate (NH_4ClO_4) has been used for decades in the United States as an oxidizer in solid propellants and explosives. The discharge of effluents from the manufacturing of this compound and from the replacement of outdated fuels in military missiles and rockets has resulted in measurable perchlorate concentrations in groundwater in several states, including California, Utah, Nevada, and Texas. Perchlorate has been manufactured, shipped, or used in at least 43 states nationwide (USEPA, 1999).

Water treatment technologies such as sedimentation, air-stripping, carbon adsorption, reverse osmosis, and advanced oxidation have not proven to be viable, cost-effective options for perchlorate removal from water (Damian and Pontius, 1999; Logan, 1998; USEPA, 1999). Unlike abiotic approaches, however, biological treatment represents a promising technology for economical removal of perchlorate from water. Several microbial strains have been isolated with the ability to degrade perchlorate to the innocuous products chloride and water (Rikken et al., 1996; Wallace et al., 1996; Coates et al., 1999). These organisms require an organic or inorganic electron donor (e.g., ethanol, acetate, hydrogen gas) for growth and utilize the perchlorate molecule as a terminal electron acceptor.

The use of biological fluidized bed reactors for the treatment of nitrate in wastewater can be traced back to the early 1970s (Sutton and Mishra, 1994). Since this time, FBR systems have been successfully applied for the aerobic, anoxic, and anaerobic treatment of a variety of chemicals in waters, including petroleum hydrocarbons, pentachlorophenol, and organic chemicals from the pharmaceutical industry. In general, an FBR system consists of a reactor vessel containing media (usually sand or activated carbon) that is colonized by active bacterial biomass. This media is "fluidized" by the upward flow of wastewater or groundwater into the vessel, with the lowest density particles (those with highest biomass) moving to the top. A control system is used at the top of the reactor to remove excess biomass, and thus control the height of the expanded media bed. The high biomass maintained within the FBR bed makes it appreciably more efficient for water treatment than many other types of biological systems, and allows reactors to be considerably smaller (USEPA, 1993).

This paper discusses the use of FBRs for the biological treatment of perchlorate in water. Results from both pilot-scale and full-scale systems are presented. Studies assessing the optimal fluidization media and most effective electron donors for perchlorate degradation in FBR systems have been reported previously (Greene and Pitre, 2000).

Objectives. The objectives of this study were (1) to assess the effectiveness of an FBR for treatment of water with a high perchlorate concentration, and (2) to evaluate operating data from a full-scale FBR system treating perchlorate in California.

MATERIALS AND METHODS

Pilot-Scale System. A process flow schematic of the laboratory pilot FBR system is given in Figure 1. Two such units were used in this study. The pilot FBRs consisted of glass columns containing sand as the fluidization media. The systems had a total liquid volume of 4 L with an empty settled bed volume of approximately 1.1 L. Each unit was equipped with automatic pH control, variable speed feed, influent and effluent pumps, water feed and collection tanks, and systems for the addition of substrates and nutrients for bacterial growth.

The water feed was introduced into the bottom of the FBR unit. Feed water was combined with recycle water from the top of the FBR prior to entering the system. Ammonia and phosphate, soluble nutrients necessary for bacterial growth, were added such that a small residual amount of each was detected in the FBR effluent. Ethanol was supplied as the electron donor for biological perchlorate destruction. The ethanol was pumped with a syringe pump into the combined feed and recycle flow (i.e., influent flow) at a dose consistent with the feed water composition, such that a small residual was detected in the FBR effluent. The sand media was added to the FBRs to yield a settled bed volume of approximately 1.1 L. The sand bed was fluidized to approximately 1.45 L using a peristaltic pump on the recycle line. The reactor pH was controlled by direct addition of caustic with a variable set point controller.

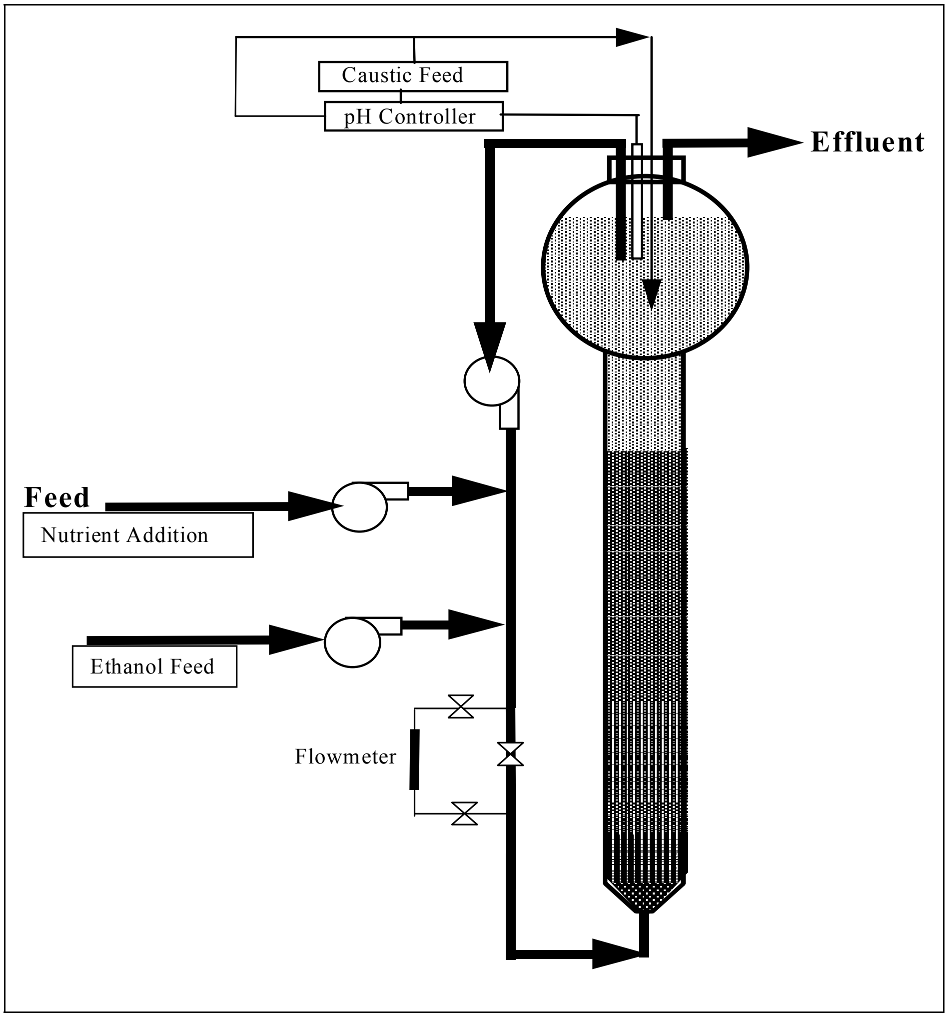

FIGURE 1. Laboratory pilot FBR flow schematic.

Water from a site in Nevada was fed to the pilot FBR units. The sand fluidization media used in the pilot FBRs came from an operating FBR system, which had been treating nitrate. FBR #1 was operated at a high loading condition, with a feed rate of 11.5 mL/min, which is equivalent to a 2.1 hour HRT (hydraulic retention time). FBR #2 was operated at a moderate loading condition with a feed rate of 8 mL/min, which is equivalent to a 3.1 hour HRT. The HRT was calculated based on the expanded bed volume and the feed flow rate to each pilot FBR. The test was conducted for 34 days at ambient temperatures (19 – 21^{o}C). A total of 132 gallons of feed water (388 reactor volumes) was processed by FBR #1 and a total of 88 gallons (270 reactor volumes) was processed by FBR #2. Levels of perchlorate, chlorate, nitrate, chloride, and sulfate were measured by ion chromatography using appropriate EPA 300.0 series methods or modifications of these methods. Total dissolved solids (TDS) were measured using EPA method 160.1.

Full-Scale System. A full-scale FBR system is currently treating water containing perchlorate at a site in California (Figure 2). The system consists of four FBRs. The FBR vessels contain granular activated carbon (GAC) as the fluidization media. The system is designed to treat a water flow of 4,000 gal/min and a perchlorate influent concentration of approximately 8 mg/L. The full-scale system is fed ethanol as an electron donor, and inorganic nutrients (N and P) are added to the influent water to support microbial growth on the GAC media. The concentrations of perchlorate, sulfate, nitrate, and phosphate the effluent water are routinely measured by ion chromatography.

FIGURE 2. Full-scale FBR system.

RESULTS AND DISCUSSION

Pilot-Scale FBRs. The average feed concentrations of perchlorate, chlorate, and nitrate during the pilot study were 400 mg/L, 480 mg/L, and 20 mg/L, respectively. In addition, the feed water contained 2,500 mg/L of chloride, 2,100 mg/L of sulfate, and total dissolved solids (TDS) of 8,200 mg/L. The objective of this pilot study was to determine whether perchlorate concentrations in effluent water could be reduced below 1.0 mg/L using a single-stage FBR. The laboratory practical quantitation limits (PQLs) of 0.2 mg/L for FBR #1 and 0.02 mg/L for FBR #2 reflect this objective. Perchlorate levels in effluent water may have been appreciably lower than these PQL values, but these levels were acceptable for the study objective.

The concentrations of the target anions, perchlorate, chlorate, and nitrate in the effluent water during the 34-day study are presented in Figure 3. For the first 3 weeks, FBR #1 was run in effluent return mode (no discharge) during biomass build-up at the high loading conditions. The FBRs were initially prepared with sand media and associated biomass from a denitrification system, so this effluent return mode was necessary to allow for a shift in the microbial biomass toward perchlorate-degrading bacteria and an appreciable increase in the total cell mass. After this period, perchlorate reduction of greater than 99.9% was achieved and effluent discharge was allowed. Perchlorate in effluent water was below the PQL of 0.2 mg/L on all but one day after the initial 21-day period. Chlorate and nitrate concentrations in the effluent were below PQLs of 1 mg/L and 1-4 mg/L, respectively, for the entire study.

For FBR #2, the effluent return (no discharge) biomass build-up mode was 14 days. After Day 18, the perchlorate concentration in effluent water was consistently below the PQL of 0.02 mg/L. Chlorate at a concentration of 300 mg/L was observed in the first effluent sample, but levels of this anion rapidly fell to non-detectable levels. Nitrate was not detected in the effluent at any point during the study.

These data show that high levels of perchlorate (400 mg/L), chlorate (480 mg/L), and nitrate (20 mg/L) in site water can be treated in a single-stage FBR system. After biomass build-up, FBR #2 consistently achieved high effluent quality, reducing all three anions below quantitation limits in effluent water. Because of the high initial loading rate, FBR #1 required a somewhat longer biomass build-up period before high effluent quality was observed. However, this unit also achieved and maintained levels of perchlorate and the other two target anions below their respective quantitation limits.

Full-Scale System. Effluent data from one full-scale FBR unit that is treating water containing perchlorate in California are presented in Figure 4. The influent flow to this FBR (feed and recycle water) during operation is maintained at approximately 1,800 gpm to provide bed fluidization. The average net feed flow of groundwater during the operational period shown was 680 gpm, but an average feed flow rate of greater than 840 gpm was maintained during the last 3 months of operation. Perchlorate levels in groundwater at the site vary from approximately 6 to 8 mg/L. The anions nitrate and sulfate are also present in the groundwater at concentrations of approximately 1.5 mg/L and 20 mg/L, respectively.

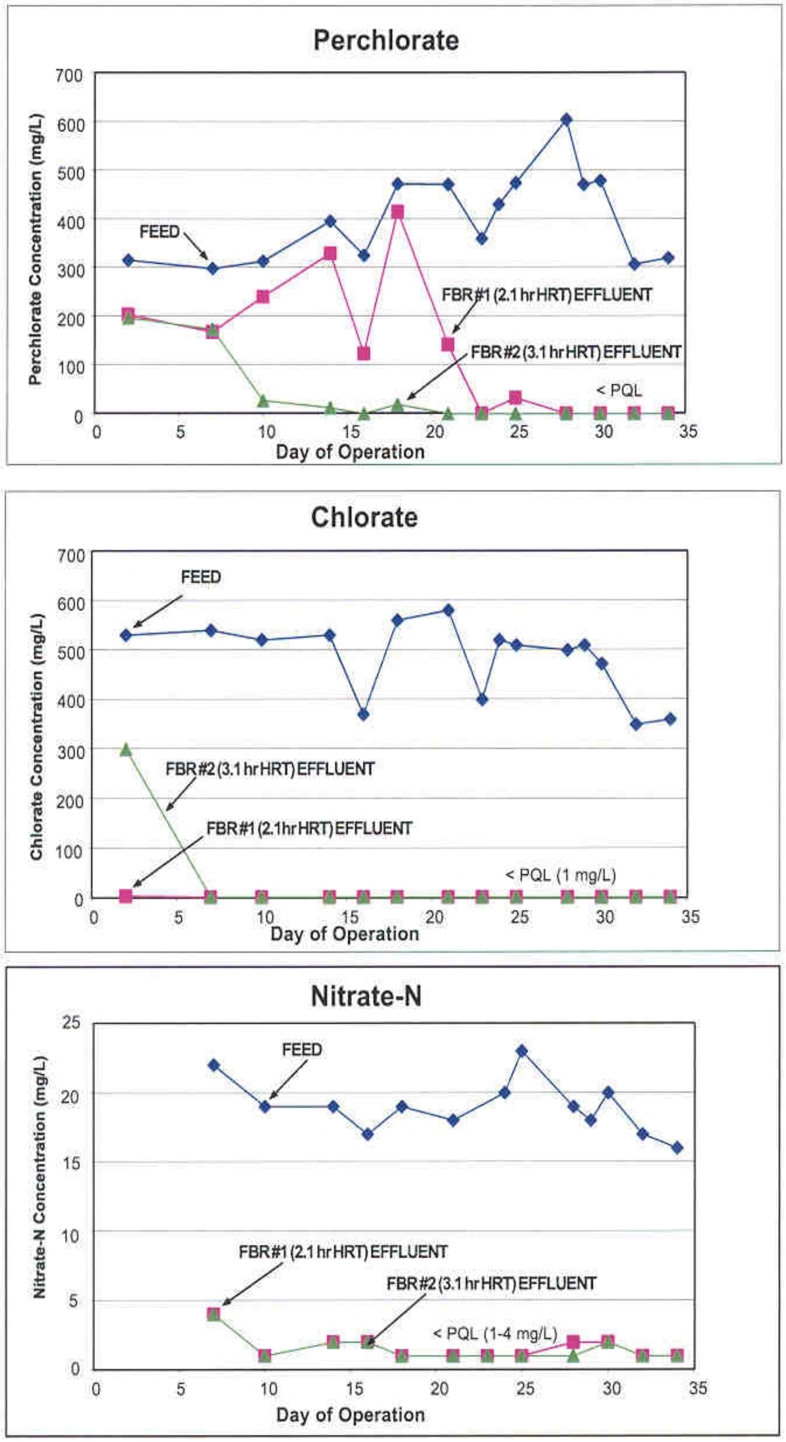

FIGURE 3. Influent and effluent concentrations of perchlorate, chlorate, and nitrate in pilot-scale FBR systems.

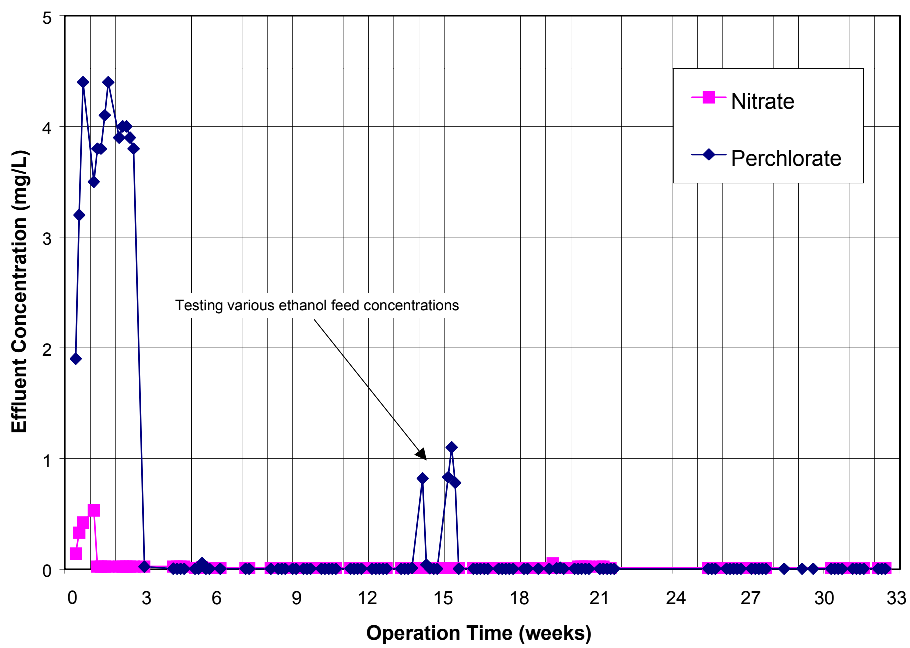

FIGURE 4. Effluent concentrations of perchlorate and nitrate in a full-scale FBR system.

The full-scale FBR system has consistently reduced perchlorate levels below the practical quantitation limit of 0.004 mg/L during the 8-month operational period. Perchlorate was detected in effluent water at a few time points during the fourth month of operation. However, system tests were being performed during this period, and the feed dose of ethanol was reduced below that required for complete perchlorate degradation. Levels of nitrate in the effluent water from the full-scale system are also consistently below detection.

SUMMARY

Perchlorate has been detected in surface and groundwater supplies in several states, including California, Nevada, Utah, and Texas. Biological treatment technologies represent the most promising alternative for effectively removing perchlorate from water supplies. However, experimental and full-scale operational data from biological treatment systems are limited. The results presented in this paper show that FBRs are an effective technology for the treatment of a range of perchlorate concentrations in water. Pilot-scale reactors containing a sand fluidization media reduced perchlorate levels in site groundwater from 400 mg/L to below quantitation limits (0.02 - 0.2 mg/L). Chlorate and nitrate were also completely degraded in these reactors. A full-scale FBR system operating in California has been treating groundwater containing 6 to 8 mg/L perchlorate to below practical quantitation limits (0.004 mg/L) for more than 8 months. Thus, biological treatment of perchlorate using FBRs appears to be a viable option for a wide variety of waters.

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