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T. M. Brouns
S. S. Koegler
W. O. Heath

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Pacific Northwest Laboratory
Richland, Washington 99352

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182

U1/U2 CRIB GROUNDWATER BIOLOGICAL TREATMENT DEMONSTRATION PROJECT

S. S. Koegler, T. M. Brouns, and W. O. Heath

Pacific Northwest Laboratory
Richland, Washington 99352

ABSTRACT

The primary objective of the biological treatment project is to develop and demonstrate a process for Hanford groundwater remediation. Bionitrification using facultative anaerobic microorganisms is a promising technology for the simultaneous removal of nitrates and organics from contaminated aqueous streams. During FY 1988, a consortium of Hanford groundwater microorganisms was shown to degrade both nitrates and carbon tetrachloride (CCl_4). A pilot-scale treatment system was designed and constructed based on the results of laboratory- and bench-scale testing. This report summarizes the results of biological groundwater treatment studies performed during FY 1989 at the pilot-scale. These tests were conducted using a simulated Hanford groundwater with a continuous stirred-tank bioreactor, and a fluidized-bed bioreactor that was added to the pilot-scale treatment system in FY 1989. The pilot-scale system demonstrated continuous degradation of nitrates and CCl_4 in a simulated groundwater.

INTRODUCTION

Liquid wastes have been generated by 40 years of Hanford Site operations. Previously, some of these wastes, which contain radioactive, hazardous, and regulated chemicals (including nitrates and organics), have been discharged to the soil column. Many of these waste components have been detected in the Hanford groundwater. Current DOE policy prohibits the disposal of contaminated liquids directly to the environment, and remediation of existing contaminated groundwaters may be required. Bionitrification using facultative anaerobic microorganisms is a promising technology for the simultaneous removal of nitrates and organics from contaminated aqueous streams.

Biological denitrification is defined as the dissimilatory reduction of nitrate (NO_3^-) to gaseous dinitrogen (N_2) and/or nitrous oxide (N_2O) by facultative anaerobic microorganisms. Prokaryotes (bacteria) are unique among microorganisms in that they can metabolize nitrates and thus exhibit the physiological mechanism of denitrification. The extent of this ability is widely distributed among the various groups of naturally occurring bacteria. Denitrifying bacteria are aerobes, preferring to use oxygen as the terminal electron acceptor in enzyme-driven metabolism. However, when their supply of oxygen is reduced, denitrifying bacteria can function anaerobically, accepting nitrate as the terminal electron acceptor in the metabolic electron-transport chain. The co-metabolic degradation of chlorinated organics such as carbon

tetrachloride (CCl_4) by facultative anaerobes has been observed (Bouwer and McCarty 1983); however, the mechanism for this type of reaction is less understood than in the case of denitrification. In a co-metabolic process the contaminant is likely degraded fortuitously by non-specific enzymes and is not used by the microorganism as a growth substrate.

The primary objective of the biological treatment program is to develop and demonstrate a process for Hanford groundwater remediation that is capable of nitrate and organic contaminant destruction. During FY 1988, laboratory microorganism tests and bench-scale kinetics tests were performed with support from the Northwest Hazardous Waste RD&D Center (NW Center). A consortium of Hanford groundwater microorganisms was obtained and shown to degrade both nitrates and CCl_4 . Denitrification rates were determined from the results of bench-scale kinetics tests using the Hanford microbial consortium and a simulated Hanford groundwater. A pilot-scale treatment system was designed and constructed based on the results of laboratory- and bench-scale testing. A detailed description of this developmental work is presented in an FY 1988 status report (Koeqler et al. 1989).

The program is currently directed at a biological treatment demonstration using contaminated groundwater from below the U1 and U2 cribs in the 200 West area of the Hanford Site. The U1 and U2 cribs received aqueous and solvent wastes containing nitrates and uranium. Analysis of groundwater samples from monitoring wells in the crib area indicate both nitrate and CCl_4 contamination, with elevated concentrations of uranium (U) and technetium (Tc). Because of the contamination from these radioactive components, a pump-and-treat system was proposed for U and Tc removal. Westinghouse Hanford Company (WHC) is currently evaluating the use of supported liquid membranes (SLM) for U and Tc removal (Hodgson 1989). In conjunction with that effort, the pilot-scale biological treatment system was developed for demonstration of denitrification and CCl_4 degradation downstream of a U and Tc removal process.

This report summarizes the results of biological groundwater treatment studies performed during FY 1989 with the pilot-scale treatment system. Pilot-scale tests were conducted using a simulated Hanford groundwater with a continuous stirred-tank bioreactor and a fluidized-bed bioreactor that was recently added to the pilot-scale treatment system.

PROGRESS IN FY 1989

A pilot-scale, suspended-growth biological treatment system was designed, constructed, and installed in FY 1988 for use in evaluating and demonstrating the applicability of biodenitrification to Hanford groundwater remediation (Koeqler et al. 1989). The pilot-scale process, using a continuous stirred-tank bioreactor, was operated in FY 1989 with a microbial consortium obtained from Hanford groundwater samples. Pilot-scale tests using a simulated Hanford groundwater demonstrated the degradation of both NO_3^- and CCl_4 . A non-inoculated control experiment was also conducted to verify the CCl_4 material balance.

In addition to the stirred-tank bioreactor, a pilot-scale fluidized-bed bioreactor was designed and constructed for testing in FY 1989 in collaboration with staff at the Oak Ridge National Laboratory. The fluidized-bed process was installed adjacent to the suspended-growth process to permit use of the same support equipment and data acquisition system. The fluidized-

bed bioreactor was inoculated with the Hanford groundwater consortium and was operated with simulated groundwater for approximately 6 weeks in late FY 1989. Denitrification studies were conducted at two different residence times for comparison to the suspended-growth process testing.

DESCRIPTION OF PILOT-SCALE EQUIPMENT

The pilot-scale biodenitrification system consists of two groundwater feed tanks; a continuous stirred-tank bioreactor; a biomass settling tank or clarifier; and pressure, temperature, off-gas, and pH monitoring and control equipment, as shown in Figure 1. During FY 1989, a fluidized-bed bioreactor was added to the biodenitrification system that uses the same feed system and process control and data acquisition equipment. The fluidized-bed bioreactor is described later.

Two 1800-L, fiberglass-reinforced plastic feed tanks supply nitrate-bearing waste water or simulated groundwater to the bioreactors. With a design feed flow rate of 240 L/day, each feed tank is capable of supplying groundwater to the bioreactors for 7 days. Automatic flow controllers and level indicators are incorporated in the feed system to ensure an uninterrupted supply of feed to the bioreactor. A concentrated acetic acid solution is also fed to the bioreactor via a low-flow metering pump from a 5-L polypropylene container. Carbon tetrachloride is added directly to the bioreactor via a syringe pump for the CCl_4 degradation tests.

FIGURE 1. Pilot-Scale Biological Treatment System

The 50-L stirred-tank bioreactor is a cylindrical, 304L stainless steel vessel that is 61 cm tall and 36 cm in diameter (see center of Figure 1). To ensure adequate agitation, the bioreactor is equipped with four internal baffles and two flat-blade impellers driven by a 0.1-kW (1/8-hp), variable-speed motor. Thermocouples and a submersible pH electrode are included for monitoring and automatic control of the reactor pH and temperature.

The reactor effluent, which contains suspended biomass, is fed to a settling vessel (clarifier) to recover the biomass for recycle and to clarify the denitrified simulated groundwater, as shown in Figure 1. The clarifier consists of both aeration and settling zones. Air is introduced through porous ceramic diffusion stones into an aeration zone of the clarifier to shift the microorganisms to aerobic metabolism and consume any residual acetate. In addition, biomass settling is enhanced in aerobic environments where the bacteria tend to agglomerate. A recycle pump returns concentrated biomass to the bioreactor.

STIRRED-TANK BIOREACTOR TESTING

The biodenitrification pilot plant was operated in a continuous mode to obtain both denitrification and CCl_4 degradation data and provide information on system operability. A control test in which the groundwater and nutrient feed streams were maintained, but biomass was eliminated, was performed to complete a CCl_4 material balance. This control test was done to determine whether biological degradation mechanisms were responsible for the observed disappearance of CCl_4 .

The composition of the simulated groundwater, shown in Table 1, was based on analysis of groundwater from the U1 and U2 crib area. The carbon-to-nitrogen (C/N) weight ratio was maintained at 2.0 through the addition of acetic acid. The sludge recycle from the clarifier to the bioreactor was maintained at a ratio (recycle flow/feed flow) of 0.4. The bioreactor temperature was controlled at $30^\circ\text{C} \pm 1^\circ\text{C}$.

Samples of the reactor feed, effluent recycle, and product streams were obtained periodically (2/week minimum), and analyzed for biomass, nitrate, and acetate concentrations. Biomass concentrations were measured by the volatile suspended solids (VSS) technique described in Standard Methods for the Examination of Water and Wastewater (APHA 1985). Nitrate concentrations were determined spectrophotometrically using a standard cadmium reduction method available from Hach Chemical Company (Loveland, CO). These nitrate analyses were confirmed using ion exchange chromatography with conductivity detection. Acetate concentration was measured using either gas chromatography with a flame ionization detector (FID) or ion exclusion chromatography with conductivity detection.

Denitrification Tests

The bioreactor was initially inoculated with the Hanford groundwater consortium using 4 L of laboratory culture. The process was operated in a batch mode through several denitrification cycles, then fed continuously with simulated groundwater at 1.0 L/h (2-day residence time). The feed flow rate was gradually increased to 6.0 L/h (8-hour residence time). The pilot-scale system was operated over a 160-day period to obtain steady-state denitrification data.

TABLE 1. Composition of Simulated Hanford Groundwater

<u>Component</u>	<u>Concentration, mg/L</u>
Na ⁺	482
Ca ²⁺	2.21
Mg ²⁺	14.0
K ⁺	13.8
Si ⁴⁺	45.0
CO ₃ ²⁻	90.6
SO ₄ ²⁻	4.04
NO ₃ ⁻	400
PO ₄ ⁴⁻	109
Cl ⁻	405
F ⁻	19.9

Figure 2 shows the NO₃-N concentration in the reactor effluent over the 160-day test period. Except for a major process upset at day 60 and several minor upsets, the bioreactor successfully produced an effluent with a NO₃-N level below the 10 mg/L drinking water standard. The upset at day 60 was caused by failure of a solenoid valve on the pH control system. Approximately 5 L of sodium hydroxide solution drained to the reactor, resulting in a rapid increase in the pH from 7.9 to greater than 11.5. By adjusting the pH and continuing feed flow, the system recovered within approximately five days.

Reactor effluent VSS concentrations are shown in Figure 3. The VSS concentration increased from less than 100 mg/L at a 2-day residence time to greater than 1000 mg/L at an 8-hour residence time. Fluctuations in VSS concentrations were caused primarily by upsets to the sludge recycle system.

Denitrification and Carbon Tetrachloride Degradation Tests

Carbon tetrachloride degradation was tested by injecting 3.5 wt% CCl₄ in methanol directly into the bioreactor using a low-flow syringe pump. The quantity of CCl₄ injected simulated approximately 200 µg/L in the groundwater. All liquid influent and effluent streams in the process were monitored during the test using gas chromatography with electron capture detector (ECD) and FID with standard purge and trap techniques. The bioreactor off-gas flowrate and CCl₄ concentration were also monitored during the test. Except for the addition of CCl₄, process conditions were maintained identical to those during the denitrification test (8-hour liquid residence time, recycle ratio of 0.4, and 30°C temperature). The effluent NO₃-N and VSS concentrations are shown in Figure 4 for the 75-day CCl₄ test. Minor upsets caused by an interrupted sludge recycle pump resulted in low VSS concentrations several times during the test period.

Steady state was achieved between days 60 and 70 of the CCl₄ test, as determined by steady flow rates and NO₃-N and VSS concentrations. During this period, the microorganisms successfully degraded ~93% of the CCl₄ within the

FIGURE 2. Bioreactor Effluent Nitrate Concentration During 160-day Test

FIGURE 3. Bioreactor Effluent Volatile Suspended Solids Concentrations During 160-day Test

FIGURE 4. Bioreactor Effluent Volatile Suspended Solids and Nitrate Concentrations During the 75-day CCl₄ Test

bioreactor. Most of the remaining CCl₄ was air stripped in the clarifier, for an overall removal efficiency of 99.5%. The CCl₄ concentrations in the bioreactor and clarifier effluent for the 75-day test are shown in Figure 5.

At the conclusion of the CCl₄ test, a control experiment was conducted in which the simulated groundwater and CCl₄ feeds were maintained, but the biomass had been flushed from the bioreactor. All process influent and effluent streams were monitored for CCl₄ as previously described. The test approached steady state at 32 hours (four liquid residence times), as indicated by effluent concentrations. As shown in Figure 6, greater than 95% of the CCl₄ was accounted for in this test. The results from this control experiment help confirm that the biological degradation mechanism is responsible for the disappearance of CCl₄ in earlier tests.

DESCRIPTION OF FLUIDIZED-BED PROCESS EQUIPMENT

A pilot-scale fluidized-bed bioreactor, shown in Figure 7, was constructed of glass pipe, with a 1.5-L fluidized-bed section and a de-entrainment section (expansion zone) equipped with an overflow clarifier. Most of the denitrification occurs in the fluidized-bed section. The overall liquid volume of the fluidized-bed reactor was measured as 15.5 L. The fluidized-bed section consisted of a 3.8 cm inside diameter (ID) glass pipe that was 120 cm tall. The reactor was equipped with sampling ports at the top and middle of the bed. Anthracite coal, 65-80 mesh (.175-.208 mm), was used as the support bed prevented the bio-particles from falling back into the feed line.

FIGURE 5. Concentration of CCl_4 in the Bioreactor and Clarifier Effluent During the 75-day CCl_4 Test

FIGURE 6. Material Balance for CCl_4 Based on Steady-State Testing and a Noninoculated Control Test

FIGURE 7. Fluidized-Bed Biological Treatment Process

The fluidized-bed process was instrumented with pressure, temperature, off-gas, pH and flow monitoring equipment. Type-K thermocouples were used to monitor temperatures in the feed stream, the bed of bio-particles (reaction section), the expansion section, and the effluent stream. The feed and effluent pH were also monitored. An acetic acid solution was pumped directly into the groundwater feed stream immediately before the stream entered the bioreactor. The pH of the acetic acid solution was adjusted to ensure that the feed pH was greater than 6.5 and a C/N ratio of 2.0 was maintained. External heaters, connected to a temperature control unit, were used to preheat the groundwater feed to maintain an average fluidized-bed temperature of 30°C. The off-gas, containing nitrogen (N₂) and carbon dioxide (CO₂), was vented to the atmosphere. The off-gas flowrate was measured with a wet-test meter.

Samples of effluent and internal process streams were collected periodically to determine VSS, NO₃-N, and acetate concentrations. Because of the volatility of coal, VSS measurements were made using two bed samples of equal volume. One sample was sonicated and rinsed several times to remove all attached biological solids. The true biomass VSS was calculated as the difference between the VSS of the column sample and the VSS of the sonicated split sample. Four sampling ports allowed sampling of the groundwater feed, the bioreactor effluent, and the recycle stream, in addition to those samples obtained through the two fluidized-bed sampling ports.

FLUIDIZED-BED BIOREACTOR TESTING

The fluidized-bed bioreactor was inoculated with approximately 2 L of the Hanford groundwater consortium (8 g VSS) and 0.3 L (270 g) of anthracite coal. To promote initial growth of the microorganisms on the coal particles, the process was operated in a batch mode using total recycle. Following this start-up period, the fluidized-bed process was operated continuously to obtain denitrification rate data.

To maintain fluidization of the bio-particles, a superficial velocity of 0.5 to 1.0 cm/sec through the column was required. Therefore, at a feed flow rate of 6.0 L/h, a recycle flow rate of approximately 26 L/h was used to maintain a sufficient superficial velocity. During start-up of the bioreactor, clumping of bacteria and coal in the reaction section of the column resulted in repeated loss of fluidization and high levels of nitrate in the effluent. The clumping was attributed to large films of biomass on the coal particles. Recycling of coal through a vibrating screen or centrifugal pump would reduce the biofilm thickness; however, the design of the bioreactor did not allow for bio-particle recycle. A gas sparge was added to the bioreactor base and controlled by a solenoid valve and timer. A nitrogen gas (20 psig) sparge for 10 seconds every hour resulted in dramatic improvement in the bioreactor operation.

The fluidized-bed bioreactor operated at steady-state, as determined by steady flow rates and NO₃-N and VSS concentrations, for approximately 12 days at a 6.0 L/h (2.6 h residence time) feed flow rate. Effluent NO₃-N concentrations were less than 1.0 mg/L while VSS concentrations averaged 17.4 g/L. The feed flow rate was increased to 12 L/h (1.3 h residence time) and operated for seven days. An initial increase in the reactor effluent NO₃-N concentration was observed; however, within 24 hours the NO₃-N concentration had returned to less than 1.0 mg/L. At the higher feed flow rate, the VSS concentration increased to an average of 22.5 g/L.

Results of steady-state testing of the fluidized-bed bioreactor indicate that the bioreactor should be considered for full-scale demonstration of U1/U2 groundwater treatment. The fluidized-bed bioreactor has the potential to greatly reduce the size of reactor needed for a large-scale pump-and-treat biodenitrification process. The pilot-scale, fluidized-bed treatment system will be modified to permit recycle of the bio-particles. Operational tests will be conducted to ensure that the fluidized-bed bioreactor can be used for the pilot-scale groundwater treatment demonstration.

PLANS FOR FUTURE YEARS

A pilot-scale groundwater treatment demonstration with U1/U2 groundwater is scheduled for FY 1990 and 1991. The pilot-scale process will be upgraded to accommodate actual groundwater contaminated with nitrate, CCl_4 , and radionuclides such as uranium and technetium. An SLM process will be incorporated in the pilot-scale system for removal of radionuclides prior to biological treatment. All activities conducted with contaminated groundwater will require permitting and approval from the Department of Energy (DOE), Washington State Department of Ecology (WDOE), and the Environmental Protection Agency (EPA). The pilot-scale system will be permitted as a treatment, storage, and disposal (TSD) facility as required by state and federal regulations.

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