Perchlorate Reduction Using Fine Media Fluidized Bed Bioreactor with Oxidation-Reduction Potential-Based Feed Control

Chapter 2

PERCHLORATE REDUCTION USING FINE MEDIA FLUIDIZED BED BIOREACTOR WITH OXIDATION-REDUCTION POTENTIAL-BASED FEED CONTROL

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ABSTRACT

Certain bacteria, prevalent in the environment, use perchlorate as an electron acceptor and reduce it to chloride under anaerobic conditions. To develop an ex-situ treatment system for perchlorate-contaminated groundwater, we performed bench-scale test using a fine media fluidized bed reactor (FMFBR; 0.5-ft diameter, 8-ft high) inoculated with a perchlorate-reducing culture. The system was operated under anaerobic conditions. A perchlorate-water solution was introduced into a recirculating stream in the FMFBR at an upward velocity of 16 cm/min. Acetate (acetic acid) was fed as an electron donor. The objective of this study was to establish a minimal acetate feed ratio for sufficient perchlorate reduction by monitoring oxidation-reduction potential (ORP) and, consequently, to prevent ORP from falling to a range of sulfate reduction, and to limit the biomass growth from excess acetate.

The FMFBR was able to degrade 3000 - 5000 μg/*l* perchlorate to less than 4 μg/*l* in a single pass (16 min empty bed contact time) without excessive hydrogen sulfide production, when effluent ORP (vs. Ag/AgCl) was -290 - -410 mV. Accurate feed control is essential since an imbalance in acetate feed ratio results in unreacted perchlorate or sulfide production. A base feed pump was used to provide 80 % of the acetate required and an ORP controller was used to trim and balance the feed rate using a second pump. The second feed pump was activated when effluent ORP rose to or above -315 mV and deactivated when it fell to or below -320 mV. Some oscillation of effluent ORP was observed, but perchlorate was not detected in the effluent when the oscillation was kept relatively small. Average acetate feed ratio was approximately 1.1-times stoichiometry. For more stable perchlorate degradation, we will examine an

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earlier ORP detection in the bioreactor column and a more flexible control method for acetate feed.

Keywords: perchlorate, groundwater, remediation, fine media fluidized bed bioreactor, oxidation-reduction potential (ORP)

1. INTRODUCTION

Perchlorate (ClO_4^-), an anion which forms perchlorate salts such as ammonium perchlorate (NH_4ClO_4), is a potential thyroid gland toxin and a widespread environmental contaminant. Perchlorate salts have been manufactured and used as an oxidizer component for explosives such as rocket/missile fuels, fireworks and safety flares (Motzer, 2001). Perchlorate is also known to occur naturally in some areas, especially arid and semi-arid region (Rajagopalan et al., 2006, Rao et al., 2007), and Chilean nitrate fertilizer (Urbansky et al., 2001). Perchlorate salts are generally highly soluble, and perchlorate anion is very mobile in aqueous phase (Motzer, 2001, Urbansky and Brown, 2003). Perchlorate has been found in water and soil throughout the United States (USEPA, 2005a); the chemical has been detected at nearly 270 sites, more than 45 of which are on the U.S. EPA's National Priority List (USEPA, 2009). Some states have set drinking water standards for perchlorate such as California (6 μg/*l*) (CalDPH, 2007) and Massachusetts (2 μg/*l*) (MassDEP, 2006), stricter than the recently issued interim health advisory level by the U.S. EPA (15 μg/*l*) (USEPA, 2008).

Despite its persistency in the environment, perchlorate can be used as an electron acceptor by certain bacteria under anaerobic conditions and reduced to innocuous chloride. Perchlorate-reducing bacteria have been isolated from various environments (Bruce et al., 1999, Coates et al., 1999, Herman and Frankenberger, 1999, Logan et al., 2001, Rikken et al., 1996, Wallace et al., 1996, Waller et al., 2004, Zhang et al., 2002). Oxidation of electron donors, such as acetate or hydrogen, is coupled to perchlorate reduction. When acetate was used as an electron donor, the following reaction takes place: $ClO_4^- + CH_3COO^- \rightarrow Cl^- + 2HCO_3^- + H^+$ (Rikken et al., 1996). Most perchlorate-reducing bacteria also utilize oxygen and nitrate, but not sulfate, as electron acceptors (Coates et al., 1999, Herman and Frankenberger, 1999, Logan et al., 2001, Rikken et al., 1996, Zhang et al., 2002). Microbes, including perchlorate-reducing bacteria, use oxygen, nitrate in that order of preference due to the energy gained from the reactions. The energy gained from perchlorate reduction is slightly higher than nitrate reduction/denitrification (Rikken et al., 1996), although previous studies demonstrated that nitrate reduction occurred either preferentially over or simultaneously with perchlorate reduction in batch systems (Bardiya and Bae, 2005, Chaudhuri et al., 2002, Gal et al., 2008, Herman and Frankenberger, 1999,

Nozawa-Inoue et al., 2005, Tan et al., 2004, Tipton et al., 2003). As anaerobic reactions progress, microbes, but not perchlorate-reducing bacteria, use sulfate as an electron acceptor.

Due to the microbial ability of perchlorate reduction, bioremediation technologies are promising for treating perchlorate contaminated water and soil. For ex-situ bioremediation of perchlorate-contaminated groundwater, biofilm reactors, such as packed bed, fluidized bed, and membrane reactors, have been developed and tested (Brown et al., 2005, Fuller et al., 2007, Hatzinger, 2005, Min et al., 2004, Nerenberg et al., 2003, USEPA, 2005b, Zhang et al., 2005). Of these types, fluidized bed reactors (FBR) have been applied for perchlorate treatment of groundwater in commercial scale at several sites (Hatzinger, 2005). In FBR, microbes are confined by adherence to particulate media, such as sand and granular activate carbon. The media are fluidized by upward flow of water. An organic electron donor such ethanol or acetate is typically provided to the FBR for reducing perchlorate. Overfeeding the electron donor, however, results in undesirable sulfate reduction, in which sulfide is produced, and overproduction of biomass solid.

In this study, we developed a fine media fluidized bed reactor (FMFBR) system for treating perchlorate-contaminated water. An FMFBR provides a large surface area for bacteria to adhere and can be operated in a plug flow mode hydraulically, which are important characteristics to carry out a high treatment efficiency with a low contaminant concentration (Weaver, 2006). The FMFBR, operated under aerobic conditions, has successfully been applied to treatment of MTBE/TBA-containing groundwater (O'Connell and Moyer, 2007). The reactor was modified for anaerobic treatment of perchlorate, in this study. A lab pilot-scale bioreactor was constructed to develop optimal operational conditions for perchlorate degradation. Effluent water was recirculated to provide a proper fluidization of the bed. A nitrogen purge was used to remove the CO_2 produced and to maintain anaerobic conditions. The oxidation-reduction potential (ORP) of the bioreactor influent/effluent was monitored to find an optimal range for perchlorate reduction. Use of ORP to balance the feed ratio of an electron donor (acetate) to perchlorate was tested to minimize sulfate reduction as well as solid production.

2. MATERIALS AND METHODS

2.1 Enrichment of Perchlorate-Reducing Culture

Perchlorate-reducing culture was developed from anaerobic digester sludge obtained from a wastewater treatment plant in South Orange County in California.

Two liters of a culture was prepared by mixing 400 m*l* of the anaerobic sludge in a growth culture medium containing perchlorate, acetate, and nutrients (NPK and trace minerals containing molybdenum (Bruce et al., 1999)) in a 2-*l* Erlenmeyer flask. Perchlorate concentration (in the 2-*l* culture) was 10 mg/*l* (0.1 mM). Acetate added to the culture was 120 mg/*l* (2.0 mM) initially, then decreased to 12 mg/*l* (0.2 mM), corresponding to 2-times stoichiometry of perchlorate reduction. When other electron acceptors, such as oxygen and nitrate, were present, acetate concentration was raised up to 30 mg/*l* (0.5 mM). Amounts of nutrients were changed in proportion to the acetate concentration: for 12 mg/*l* acetate, 4.3 mg/*l* NH_4Cl, 0.98 mg/*l* Na_2HPO_4, and 0.34 mg/*l* KH_2PO_4 were added. pH was adjusted to 7.0 - 7.2 using NaOH. The headspace was flushed with nitrogen (N_2) gas and the flask was closed with a rubber stopper. The culture was stirred slowly and incubated at 22 - 32 °C. When perchlorate was degraded < 1 mg/*l*, stock solutions of the chemicals were added again. From time to time a portion of the culture solution was discarded and replaced with fresh culture medium to remove accumulated salts.

2.2 Bioreactor Design and Operations

The FMFBR system consisted of a 12-gal (45-*l*) FMFBR column, a countercurrent gas-liquid packed column, and a 30-gal (113-*l*) equalization tank (Figure 1). The clear PVC FMFBR column was 6 inches in diameter and 98 inches high. Approximately 6 gallons (bulk volume, about 4 feet high in the FMFBR when settled) of fine silica sand was filled in the FMFBR column. Water was drawn from the equalization tank at a flow rate of 0.75 gpm (2.8 *l*/min) using a centrifugal pump and a flow control valve. The water was injected through a PVC pipe inserted in the center of FMFBR column and dispersed at the bottom through three holes, creating an upward flow for fluidization of the bed. The hydraulic loading rate was 3.8 gpm/ft^2 (upward velocity 16 cm/min), and the empty bed contact time was 16 min. The expanded bed height was 80 - 96 inches.

The water passed through the FMFBR and overflowed to the packed column which was 4 inches in diameter, 48 inches tall. The column was packed with a plastic filter medium and was purged with N_2 gas (1.5 - 2.0 *l*/min) to remove CO_2 produced by oxidation of acetate. The treated water was recycled to the equalization tank, where feed materials were added and spent solution was withdrawn.

Figure 1. Anaerobic fine media fluidized bed bioreactor system.

2.2.1 Start-Up and ORP Monitoring

As an inoculum for the FMFBR, 2 gallons of the batch culture was added to the stream so the microbes attach to the surface of the fine media while the liquid was recirculating. Perchlorate was added to the tank in batch mode for the first two months. The equalization tank was monitored for ORP, pH and perchlorate concentration. Acetic acid (10 - 100 mM (600 - 6000 mg/*l*)) was fed continuously to the bottom of the FMFBR at an average rate of 3 *l*/d using a metering pump. Nutrients were mixed with acetic acid (for 10 mM acetate, 215 mg/*l* NH_4Cl, 31 mg/*l* Na_2HPO_4, 34 mg/*l* KH_2PO_4, trace mineral solution) first, but due to biomass growth in the feeding stock even at the low pH (~3.6), they were added in batch mode later.

Bioreactor operation was then switched to continuous mode. Concentrated perchlorate (5000 - 10000 mg/*l* (50 - 100 mM)) was loaded to the equalization tank at a rate of 1.5 - 1.7 *l*/d by using a metering pump and mixed with the recycled liquid. Influent perchlorate concentration to the FMFBR was incrementally increased from 3 to 7 mg/*l*. Acetate feed rate was balanced with

perchlorate loading rate by manually adjusting the metering pump flow rate. NPK and trace minerals were also continuously provided with perchlorate and acetate, respectively. Bioreactor effluent ORP was monitored at the FMFBR outlet, before entering the gas-liquid packed column. Another ORP probe was later installed in the equalization tank to monitor influent ORP. Influent pH was also monitored in the tank.

2.2.2 Operation Using ORP-Based Feed Control

Two acetate feeders (75 - 100 mM each) were used to provide variable feed rates based on the change in effluent ORP. The first (base) acetate feeder provides nominal 80 % (actual 70 – 80 %) of perchlorate feed rate constantly. The second acetate feeder was controlled by an ORP controller (model 6311, Jenco Instruments, San Diego, CA) monitoring effluent ORP: the feed pump was activated when effluent ORP elevated to a high ORP set point and deactivated as the ORP lowered below the set point. The high set point used in this study was -300, -315, and -330 mV and the hysteresis value was 5 mV. Influent ORP (in the tank) was also monitored with an ORP probe and an ORP controller (model 3679N, Jenco Instruments). Influent perchlorate concentration was 2.3 - 3.6 mg/*l*.

Acetate injection point was changed to the pipe between the centrifugal water pump and the flow control valve to ensure mixing of acetate in the stream before entering the FMFBR column. This is because ORP changes and perchlorate degradation data suggested acetate was not mixed with the stream completely in the FMFBR when injected to the bottom, causing the delay in the response with the ORP-control mode. Influent pH was adjusted to 7.2 - 7.4 using NaOH to minimize effects of pH on ORP, though N_2 sparging at a flow rate of 1.8 - 2.0 *l*/min well maintained the pH in this range and the necessity of NaOH addition was minimal. Effluent pH before N_2 sparging was 0.15 - 0.17 lower than influent pH.

2.2.3 Measurement of Sulfide Production with Sulfate Loading

Sulfide production during the ORP oscillation was analyzed. Some sulfate was present in the tap water used but the amount was small and variable. Therefore, sodium sulfate (50,000 mg/*l* (= 520 mM) as SO_4^{2-}) was mixed with perchlorate solution and loaded to the equalization tank. Sulfate concentration added to the stream was approximately 20 mg/*l*. Estimated cumulative sulfate at the time of the samplings was 120 g, corresponding to 840 mg/*l* sulfate increase in the system (A semi-quantification showed a larger sulfate concentration probably due to sulfate carried over from tap water). N_2 sparging of effluent was stopped during the sampling not to purge H_2S out of the water. Influent pH decline during the sampling was small (-0.02). Influent perchlorate concentration was 2.6 - 3.4 mg/*l*.

Acetate feed rate was controlled based on effluent ORP measurement as described above, with the high ORP set point of -315 mV.

2.3 Analytical Methods

Perchlorate concentrations higher than 1 mg/*l* were measured using a perchlorate ion selective electrode (Cole-Parmer, Vernon Hills, IL) equipped with a multiparameter meter (5-Star benchtop meter, Thermo Scientific Orion, Beverly, MA). Perchlorate concentrations less than 1 mg/*l* were analyzed by ion chromatography (IC; analyses were performed by Calscience Environmental Laboratories, Inc., Garden Grove, CA), according to EPA method 314.0. The reporting limit was 2 μ g/*l*, though sample matrix interferences raised the limit to 4 - 20 μ g/*l*.

The ORP probe used in this study was a platinum-Ag/AgCl combination electrode (M-10-ORP, Endress+Hauser Conducta, Inc., Anaheim, CA). The values were indicated against Ag/AgCl, which are 200 mV smaller than against standard hydrogen electrode. pH 4 and 7 buffers saturated with quinhydrone (263 mV and 86 mV at 25°C, respectively) were used to check the calibration of ORP probes. pH was measured with a combination pH electrode (M-10, Endress+Hauser) equipped with the multiparameter meter. Dissolved oxygen (DO) was analyzed with a DO meter (model 55, YSI Inc. Yellow Springs, OH).

Sulfide concentrations in the liquid samples were measured using hydrogen sulfide test kit (model HS-C, Hach Company). Test strips were also used to measure concentrations of nitrate + nitrite (Hach Company) and sulfate (EMD chemicals) semi-quantitatively.

3. RESULTS

3.1 Perchlorate Degradation by Batch Enrichment Culture

With the anaerobic sludge as an inoculum, the batch culture degraded over 90 % of 10 mg/*l* perchlorate in less than 5 days. The culture soon became capable of degrading perchlorate from 10 mg/*l* to an undetectable level (< 2 μg/*l*) within 2 - 3 days. The culture also consumed nitrate and DO when they were present.

3.2 Perchlorate Degradation and ORP Changes in the Bioreactor

3.2.1 Perchlorate Degradation and ORP during the Startup of the Bioreactor

When starting up the FMFBR, about three days was needed to degrade more than 90% of 10 mg/*l* of perchlorate, probably due to the small density of perchlorate-reducing bacteria. As batch perchlorate degradation repeated, the degradation rate became much larger, suggesting the growth of perchlorate-reducers in the bioreactor. The ORP of the recirculating water was -200 - -270 mV when perchlorate concentrations were larger than 1 mg/*l*. As perchlorate was degraded to less than 1mg/*l*, the ORP dropped below -280 mV (down to -500 mV observed), and the bioreactor started generating sulfide and volatile fatty acid odors. The pH was 7.5 - 8.3 with no acid-base control.

3.2.2 Perchlorate Degradation and ORP Changes in Continuous Mode

In continuous mode, perchlorate (3 - 7 mg/*l*) was degraded to less than 1 mg/*l* in a single pass, provided that acetate feed rate was sufficient. IC analysis of the effluent samples confirmed the FMFBR was capable of degrading 4 - 5 mg/*l* of perchlorate to below 4 μ g/*l* in a single pass.

Small shifts in the feed ratio, however, often led to either overfeeding or underfeeding of acetate. The overfeeding caused a further decline in ORP toward sulfate reduction range, generating hydrogen sulfide; on the other hand, the underfeeding of acetate led to accumulation of perchlorate in the bioreactor. Our observations show that when the feed ratios produced effluent ORP in the -230 to -290 mV range, perchlorate was not completely degraded (Figure 2, right). To obtain effluent perchlorate values less than 1 mg/*l*, acetate feed rate had to be increased until the ORP dropped below -290 mV (Figure 2, middle). When acetate was overfed, effluent ORP dropped to less than -420 mV, acetate carried over into the surge tank initiating reactions there and a hydrogen sulfide smell was noted (Figure 2, left). The feed ratios producing effluent ORP of in the range of -290 to -410 mV resulted in over 90% of perchlorate reduction without considerable sulfide production. Influent ORP remained -220 to -250 mV, unless the reaction occurred in the tank by the excess acetate, causing influent ORP dropping lower than -370 mV (Figure 2, left). The average molar ratio of acetate to perchlorate was approximately 1.3, higher than the stoichiometry.

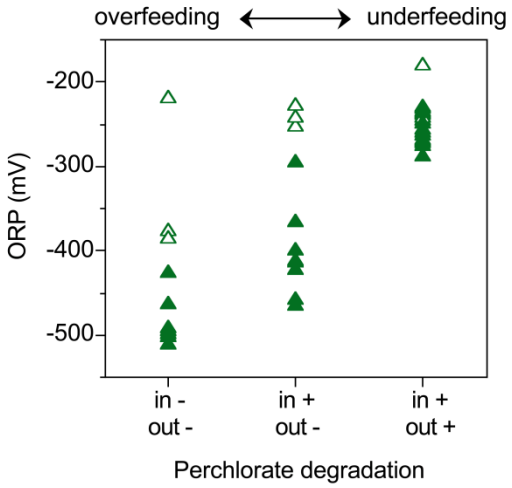

Figure 2. Relationship between perchlorate concentration changes and ORP of FMFBR influent (open triangle)/effluent (closed triangle). in + = measured influent perchlorate concentration was ≥ 50 % of the concentration estimated from the stock solution loading rate; in - = measured influent perchlorate concentration was < 50 % of the estimated concentration; out + = effluent perchlorate concentration was ≥ 1mg/*l*; out - = effluent perchlorate concentration was < 1 mg/*l*.

3.3 Perchlorate Degradation with ORP-Based Acetate Feed Control

3.3.1 Effect of Acetate Feed Rate on ORP Changes and Perchlorate Degradation

Based on the effluent ORP targets of -300 to -350 mV, a feed control system was set up with a base rate of acetate feed approximately equal to 80% of stoichiometry, and the balance being fed with a second pump (trim pump) adjusted based on the ORP detected at the exit from the fluidized bed. In the first set of experiments with the high ORP set point of -300, -315, and -330 mV, the flow rate of the trim pump, when activated, was approximately three times larger than that of the base acetate pump. Large oscillations of effluent ORP were observed in this set (Figure 3 a~c). After effluent ORP rose to the set point and the second acetate feed pump started running, the ORP elevated further for 12 ± 2 min, then declined below the set point. The ORP kept falling further for 13 ± 3 min even after the second pump stopped. Oscillation of influent ORP was much smaller than that of effluent ORP. The delay in the response of effluent ORP was likely caused by the travel time of the liquid from the acetate injection point to the bioreactor outlet, in particular, the bioreactor hydraulic retention time. Overall molar acetate feed ratio to perchlorate was approximately 1.2. Although the ratio indicated acetate was still fed in excess, the ratio was lower than the number observed without ORP control. Effluent perchlorate concentrations around the

second peak of effluent ORP curves were below 1 mg/*l*, but 400 and 180 μg/*l* of perchlorate was detected at the highest ORP by IC analysis with the set points of -300 and -330 mV, respectively (Figure 3 a and c). Perchlorate was not detected (< 4 μg/*l*) at the peak of ORP with the set point of -315 mV (Figure 3 b).

By lowering the flow rate of the second pump when activated and, consequently, decreasing the amount of acetate used for trim, the oscillations were damped considerably, especially with the high ORP set point of -315 mV (Figure 3 d and e). The molar acetate feed ratio to perchlorate decreased to 1.1. Perchlorate was not detected (< 4 μg/*l*) in the effluent with the high ORP set point of -315 mV (Figure 3 d). With the set point of -330 mV, 240 μg/*l* of perchlorate was detectable in the effluent at the second peak of effluent ORP (Figure 3 e). Although effluent perchlorate concentrations were undetectable (< 4 μg/*l*) at the peaks of effluent ORP curves in both experiments with the set point of -315 mV (Figure 3 b and e), repeated experiments revealed perchlorate was often detectable in effluent when the ORP oscillating more than observed in Figure 3d. Suppressing the oscillation appeared to be important to achieve sufficient perchlorate reduction.

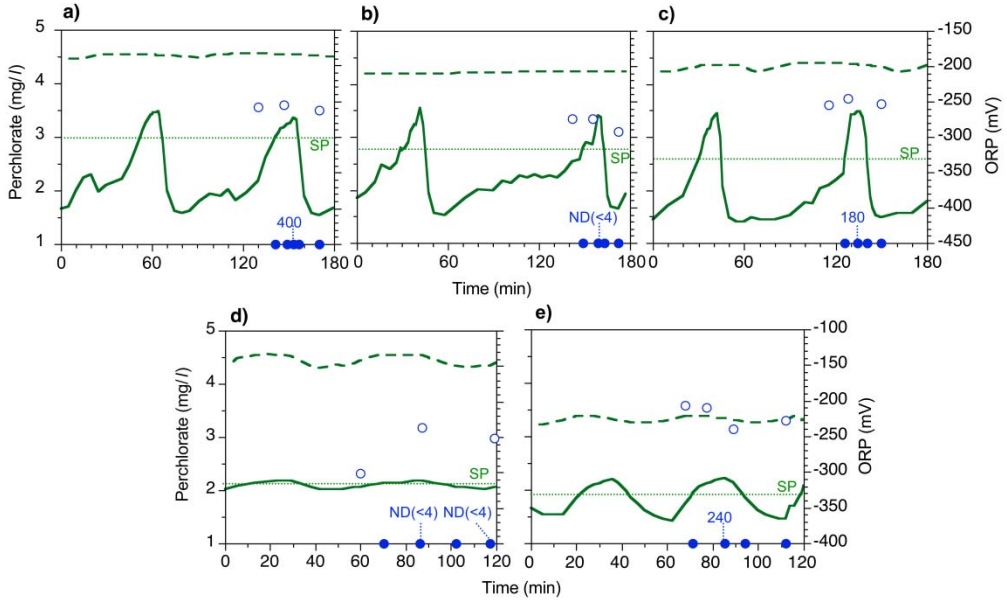

Figure 3. Changes in influent (broken line)/ effluent (solid line) ORP and influent (open circle)/effluent (closed circle) perchlorate concentrations. Perchlorate concentrations with values were analyzed by ion chromatography (unit: μg/*l*, ND = not detected). High ORP set points (indicated as "SP" and dotted line) used for the second acetate feeder activation were -300 mV (a), -315 mV (b and d), and -330 mV (c and e). The second acetate feed pump flow rate when activated was approximately 3x (a~c) or 1x (d and e) the base feed pump flow rate.

3.3.2 Sulfide production during ORP oscillation

Despite the continuous sulfate loading, hydrogen sulfide was not detected (< 0.1 mg/*l*) in the effluent samples around the second peak and bottom of the ORP curve, even at the lowest ORP (-325 mV) (Figure 4). Effluent ORP oscillation was very small in this experiment. Perchlorate was degraded to an undetectable level (< 20 μ g/*l*; a higher reporting limit due to the sample matrix interference).

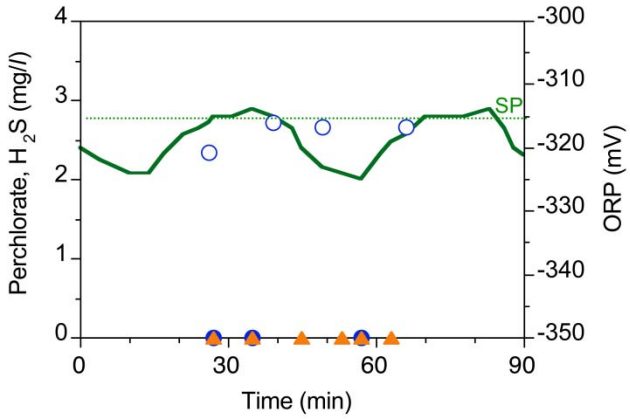

Figure 4. Changes in effluent hydrogen sulfide concentrations (closed triangle) and influent (open circle)/effluent (closed circle) perchlorate concentrations during a cycle of the second acetate feeder activation and deactivation. The solid line shows effluent ORP. The high ORP set point (shown as SP and dotted line) was -315 mV.

4. DISCUSSION

The bioreactor system has successfully degraded perchlorate to less than 4 μ g/*l* in a single pass. The anaerobic sludge used for the batch culture quickly gained the ability to degrade perchlorate, as expected from a previous study (Attaway and Smith, 1993). The inoculum (batch culture) was also capable of utilizing nitrate and oxygen. We did not monitor DO and nitrate in the FMFBR except the start-up period because the amounts provided to the stream were very small, although those electron acceptors would be consumed if present. Removal of oxygen can be done by purging or vacuum extraction, whereas nitrate may need to be treated together with perchlorate by providing sufficient electron donors. Care must be exercised, however, to limit the feed rate of electron donors to that required for perchlorate (and nitrate) reduction, in order to stop the anaerobic process before the reduction of sulfate to hydrogen sulfide.

Although perchlorate reduction appeared to occur over a range of redox potential or ORP which includes nitrate reduction/denitrification, the detailed

ORP data associated with perchlorate reduction activity are limited. Shrout and Parkin (2006) found perchlorate was completely degraded at -420 mV (vs. Ag/AgCl) but only partially degraded at or above -250 mV in their batch experiment. Our results in the continuous operation (without ORP control) were consistent with their results: although a partial degradation was observed at a higher ORP, complete perchlorate degradation was only observed when effluent ORP lower than -290 mV. The threshold value for complete perchlorate reduction was also well above the starting point of major sulfide production (by sulfate reduction), -350 mV (Connell and Patrick, 1968).

Our experiments confirmed that overfeeding the electron donor in a perchlorate treatment process produces sulfide. As effluent ORP dropped below -420 mV by continuous acetate overfeeding, a strong hydrogen sulfide odor was generated from the reactor and the color of the liquid turned black. Metal sulfides also appeared to be accumulated, causing the bed volume increase. When the reactor was operated under ORP control and acetate feed was limited, only a faint smell of hydrogen sulfide was detectable from the packed column gas outlet as effluent ORP declined below the set point. This level was not detectable by the hydrogen sulfide test kit, suggesting only ppb level of hydrogen sulfide was generated during the ORP decline.

Solid production increased dramatically when the acetate was overfed. Ideally, electron donor/carbon feeding should be limited to achieve near zero net growth of biomass to reduce the cost of chemicals and maintenance. The ORP-based feed control was successful in reducing the feed ratio close to stoichiometry in this study. Solids in the FMFBR were produced relatively slowly: settled bed height often remained in a similar range for a few months, although expanded bed height gradually increased. However, rapid increase in the bed height was observed when ORP was very low as described above or water was exposed to air due to maintenance. Oxygen not only competes with perchlorate reduction but also effectively increases biomass in the reactor. Removal of dissolved oxygen in the incoming stream should be performed if possible.

Although perchlorate could be degraded to an undetectable level ($< 4\ \mu g/l$) in this system with ORP-feed control, effluent ORP was still oscillated and a fine adjustment of acetate flow rate was needed to perform sufficient perchlorate degradation. A typical on/off-type process control causes oscillations of the controlled variable. Using the two feeders, one of which constantly provided a major portion of acetate required, alleviated the oscillation problem. Yet, monitoring ORP at the bioreactor outlet caused a delay in detecting the ORP change. For a more stable ORP control and a better perchlorate degradation performance, the following improvements are being considered: 1) detecting ORP change earlier; 2) changing feed rate continuously depending on ORP change

using a proportional-integral-derivative (PID) control system, rather than two feed rates by turning on/off the second feeder. The earlier detection may be done by installing an ORP probe in the bioreactor column. Near the mid-point of the reactor, about 4 feet from the bottom, the peaks and the bottoms of the ORP curve came about 8 minutes earlier (data not shown). Although the ORP values were slightly lower than those measured at the outlet, the slope change in ORP curve monitored near the mid-point of the bioreactor may be used for feed speed control. PID control can be used for responding the slope change as well as a more continuous change of feed rate. We will perform these improvements and investigate if ORP oscillations are minimized; hence, perchlorate degradation performance of the bioreactor is more stabilized.

5. CONCLUSION

The FMFBR has ability to degrade 3000 - 5000 μg/*l* perchlorate to an undetectable level (< 4 μg/*l*) in a single pass of EBCT 16 min. ORP-based acetate feed control reduced the feed ratio and is promising to solve the problems derived from overfeeding such as excess solid production of the bed and sulfide production. For a stable performance of the FMFBR, a more sensitive ORP control is needed. An earlier detection of ORP in the bioreactor column and a more flexible control method of acetate feed rate such as PID control may improve the control sensitivity.

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