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Reduction of Bromate Source Contamination

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Abstract A potential source remediation technique for an aquifer contaminated by bromate has been investigated, utilising biological bromate reduction to bromide by augmentation of indigenous microbial populations. This technique, involving addition of a carbon source to contaminated groundwater, is analogous to the methodology used in commercial denitrification systems. Experimental work is aimed at development of an *ex-situ* pump-to-waste or pump, treat-and-reinject strategy, but the technique may also have *in-situ* applications. Trials initially focussed on a laboratory-scale anaerobic suspended growth chemostat system, investigating glucose addition to real groundwater supplies. Following targeted enrichment of the microbial population, reduction of 32 mgl^{-1} bromate within a 40 hour residence time was obtained with specific reduction rates of up to 160.48 µmol Br.g dry $wt^{-1}.hr^{-1}$, which suggested the presence of high-rate bromate reducing bacterial strains. Use of a pilot-scale fixed-film upflow bioreactor seeded with enriched chemostat biomass subsequently confirmed stoichiometric bromate reduction to bromide with 87-90% bromate reduced from an influent concentration of 1.08 mgL^{-1} over retention times of 40-80 hours. Nitrate reduction of 97-99% from a 30.7 mgL^{-1} nitrate (as NO_3^-) influent also occurred at retention times of 10-80 hours, although an increase in nitrite production to 2.7 mgL^{-1} was observed with a 10 hour retention time. A period of batch operation during the startup phase was shown to be critical to stable operation, but backwashing was not required during the timescale of the experimental run. Further process optimisation will be required, but this study has demonstrated the potential of biological bromate reduction for remediation of a bromate contaminated groundwater source.

Keywords Bromate, Bioreactor, Fixed-film, Groundwater, Pilot-scale

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Introduction

Water contamination by bromate (BrO_3^-), an oxyanion of bromine, is commonly associated with ozonation processes where it is formed as a disinfection by-product (DBP) of water containing naturally-occurring bromide (Br^-). It can also be produced during water treatment following addition of chemicals such as calcium chloride containing bromide as an impurity. Despite being a thermodynamically powerful oxidant, once in solution bromate is highly stable at room temperature (DSP, 1999). Following evidence of carcinogenicity (Kurokawa et al., 1986), bromate was classed as a Group 2B carcinogen by the World Health Organisation. Maximum concentrations in drinking water have now been limited to 10 μgL^{-1} in a number of countries including the UK, the United States and Canada, with European Union (EU) regulations currently stating a 25 μgL^{-1} limit until 2008 when 10 μgL^{-1} will be enforced in all EU countries.

Bromate has not historically been perceived as an environmental contaminant, and is not reported as occurring naturally in surface waters (Hutchinson et al., 1997) or aquifers. However, advances in the application of Ion Chromatography (IC) analytical techniques and the impetus of tighter legislation have together led to enhanced monitoring programmes. As a consequence, bromate has now been detected within both the surface water environment (Kruithof and Meijers, 1995) and more recently within a chalk aquifer in the UK. Significant bromate contamination of industrial origin has led to formation of a plume within this aquifer which is currently affecting potable water abstraction in the area and has lead to an examination of possible bromate treatment methods.

Biological bromate reduction to bromide has been shown to occur according to the equation below.

$$C_6H_{12}O_6 + 4BrO_3^- \rightarrow 6CO_2 + 4Br^- + 6H_2O \quad (1)$$

Hijnen et al. (1999) demonstrated that bromate could be reduced in a denitrifying bioreactor supplemented with ethanol using both mixed and pure cultures. Although batch studies initially indicated a bromate reduction rate over 100 times lower than that of nitrate reduction (Hijnen et al., 1995), continuous flow trials showed the two rates could be comparable at similar influent concentrations (Hijnen et al., 1999). Biological bromate reduction has also been observed on Biologically Active Carbon (BAC) filters (Kirisits and Snoeyink, 1999; Kirisits et al., 2001). In neither case was reduction by specific bromate reducing strains demonstrated, and the hypothesis that nitrate and bromate competed for use as electron acceptors was put forward (Kirisits et al., 2001).

In this paper, studies are described to harness biomass acclimatised to bromate contamination within a fixed-film pilot-scale bioreactor system, for source reduction of bromate to bromide in contaminated groundwater. Two bioreactors were operated between June and October 2004, treating groundwater from a contaminated aquifer containing approximately 1 mgL^{-1} bromate influent. Following inoculation of the reactors with biomass and a 23-day period of acclimation in batch culture, the ability of the system to reduce bromate to bromide was evaluated. The effect of retention time on efficacy of the system, supplied with carbon in excess, was investigated and bromate removal rates examined.

Materials and Methods

Bioreactors

Pilot-scale trials were conducted using two identical bioreactors (Reactors 1 and 2) (Figure 1). The cylindrical reactors were operated in upflow mode and had a height of 1.4 m and internal diameter of 0.2 m. For continuous flow operation they were packed with Etapak 210 (Koch-Glitsch UK, Stoke-on-Trent, UK), a random plastic media with a diameter of 63 mm, surface area of 200 m^2m^{-3} and voidage of 96%. The media was packed within each reactor to give a bed height of 1.2 m and volume of 36 litres. Groundwater was pumped into the reactor at flow rates of 7.1 – 57.0 $mLmin^{-1}$, with nutrient stock solution added at 0.38 - 3.0 $mLmin^{-1}$ via a separate influent supply pump. The nutrient stock solution contained 2 gL^{-1} glucose as a carbon source and 2 gL^{-1} ammonium chloride (NH_4Cl) as nitrogen source (both laboratory grade; Fisher Scientific, Loughborough, UK), giving a molar C:N ratio of 1.78:1. This was added at a rate to give a groundwater:amendments dilution ratio of 20:1, and thus a 100 mgL^{-1} final influent concentration of both glucose and NH_4Cl (40.0 mgL^{-1} as C and 26.2 mgL^{-1} as N). No attempt was made to optimise addition of carbon (which was added in excess), with the aim of the study focussing on ability and performance of the reactors in removing bromate contamination. Influent flow rates gave reactor retention times of 10 - 80 hours, with mixing provided by a peristaltic pump (flow rate of 0.65 $Lmin^{-1}$) which continuously recirculated the reactor contents. Effluent flow was through an overflow with a one-way valve on the mixing line.

Influent groundwater supplies

Two groundwater supplies (GW-1 and GW-2) with elevated concentrations of bromate and bromide were obtained from a contaminated aquifer in the UK. Selected properties of the two groundwater sources, including influent anion concentrations of interest, are given in Table 1. Groundwater GW-1, utilised for initial batch operation (Phase A) only, was collected in 25L jerry cans and stored at 7^oC prior to use for up to 60 days. Groundwater GW-2 was pumped into a holding tank (1.05m^3) for transportation to the test facility and was stored within the facility at ambient temperature for a maximum of 50 days prior to use.

Table 1 - Selected properties of influent groundwater supplies (GW-1 and GW-2), and supernatant samples measured at 80 hour retention time

	GW-1*	**GW-2 ****	**Reactor 1 *****	**Reactor 2 ********
pH	6.92	7.29 ± 0.26	7.24 ± 0.30	7.31
Total Organic Carbon (mgL^{-1})	19.86	47.18 ± 2.72	14.26 ± 11.78	12.364
Bromate as BrO_3 (mgL^{-1})	1.36	1.08 ± 0.25	0.16 ± 0.11	0.14
Bromide as Br (mgL^{-1})	16.58	2.30 ± 0.41	2.78 ± 0.37	3.83
Total oxidised Nitrogen as NO_3 (mgL^{-1})	8.57	30.71 ± 4.69	< 0.25	< 0.25
Nitrite as NO_2 (mgL^{-1})	0.081	< 0.06	< 0.06	< 0.06
Sulphate as SO_4 (mgL^{-1})	74.80	24.52 ± 2.82	21.45 ± 3.88	21.10

* Single sample collected 7 May 04 ; ** n=8 (TOC: n=5); *** n=3;
**** Single sample collected 15 Sept 04; Errors given as ± 1 standard deviation

Inoculum

Inoculum was obtained from a laboratory scale chemostat system which had been in continuous flow operation for approximately 15 months with the aim of developing a bromate-reducing enrichment culture. The chemostat was operated using groundwater GW-1, which had previously been suggested to contain bromate reducing bacterial strains. Bromate reduction of up to 48 mgL^{-1} with a 40 hour retention time was observed in the chemostat system prior to transfer of inoculum. Experimental setup and chemostat operating parameters have previously been described in Butler et al. (in press). Optical density (absorbance at 600 nm) of the chemostat inoculum at time of addition was 0.055 ± 0.021.

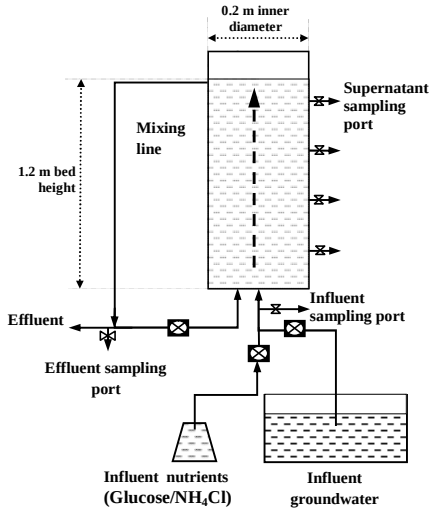

Figure 1 Schematic of upflow bioreactor

Reactor operation

The period of reactor operation was split into two phases, with an initial 23-day start-up period of batch configuration identified as Phase A (Days A0-A22), and the subsequent 98-day fixed-film continuous flow operation given as Phase B (Days 0-97). Phase A was run as a suspended growth system using reactor 2 only. Plastic media was added to both reactors for fixed-film operation on the first day of Phase B (Day 0). Within Phase B an acclimation period of 63 days (Days 0-62) was followed by the main experimental period (Days 63-97). These periods were designated phases Bi and Bii respectively.

Analytical procedures

Simultaneous analysis of all anions of interest was completed using a Dionex ICS-2500 IC system incorporating an ED50 electrochemical detector and AG9-HC guard column and AS9-HC analytical column, with a 9 mM sodium carbonate eluent, 1 $mLmin^{-1}$ flow rate and 250 µL sample injection. Errors were calculated as ± 1 standard deviation.

Results

Reactor 1

Reactor 1 was operated as the control at a retention time (RT) of 80 hours. However, it was only considered in steady state operation for days 81-97, during which period average percentage bromate and nitrate reductions within the supernatant of 85.0% and >99.2%

(below detection limit) respectively were obtained. Nitrite concentrations during this period were always below 0.06 mgL^{-1}, suggesting total denitrification to nitrogen gas was occurring at all times. Bromide supernatant concentrations were in excess of influent, with an average of 2.8 ± 0.37 mgL^{-1} during the steady state period.

Reactor 2

Reactor 2 was operated at an 80 hour RT between days 63-68, giving a comparison with the control reactor to investigate reproducibility of the system (Table 1). Percentage bromate and nitrate reduction within reactor 2 at the 80 hour RT were 87.2% and 98.1% respectively. Lower retention times of 60 and 40 hours led to little alteration in bromate or nitrate reduction, with percentage removals at 40 hours of 90.3% and 98.3% respectively. Under 20 and 10 hour retention times, minimal alteration in nitrate reduction capacity was noted (97.2% and 97.5% respectively). However, an increase in nitrite production was observed with the 10 hour retention time, leading to supernatant concentrations of 2.7 mgL^{-1}. A slight loss in bromate reduction capacity at a 20 hour retention time (80.4%) became more marked under a 10 hour retention time, leading to only 17.5% reduction. Sulphate reduction was noted at all retention times apart from 10 hours, with a maximum reduction of 15.3 mgL^{-1} at a 20 hour retention time from an influent of 24.5 ± 2.8 mgL^{-1}. Figure 2a shows bromate and bromide concentrations and Figure 2b gives nitrate, nitrite and sulphate concentrations during the experimental phase. TOC concentration in the supernatant was always >10 mgL^{-1}, indicating that carbon was not limiting at any retention time and was always in excess.

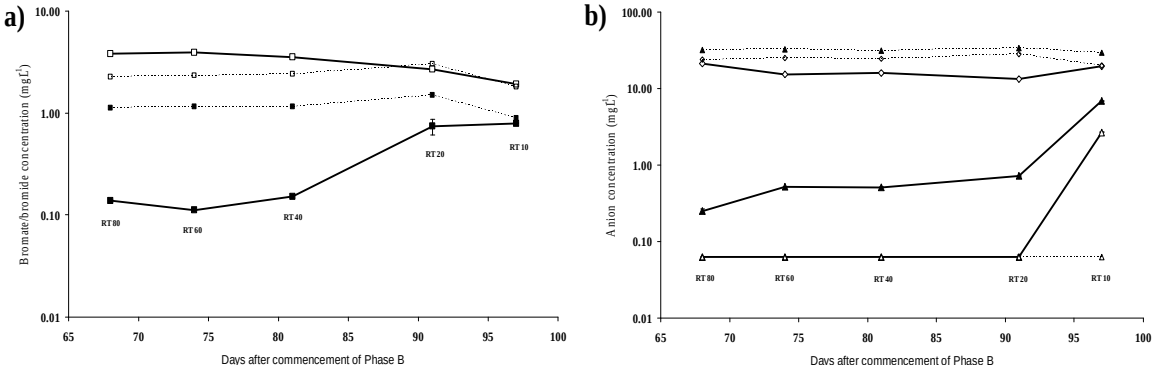

Figure 2 Reactor 2 bromate (■) and bromide (□) (Figure 2a), and nitrate (▲), nitrite (Δ) and sulphate (◊) (Figure 2b) concentrations during Phase Bii at retention times from 80 hours (RT80) to 10 hours (RT10). Supernatant concentrations indicated by solid lines (—) and influent concentrations by dashed lines (---)

Conclusions

Bromate contamination of approximately 1 mgL^{-1} within real groundwater samples was successfully removed by biological reduction to bromide using acclimatised biomass in a fixed-film upflow bioreactor with ambient temperature and addition of only a simple glucose/NH_4Cl mixture as nutrient source. Bromate was stoichiometrically reduced to bromide, with an optimum retention time of 20-40 hours required leading to reduction of 80-90% influent bromate. A lower retention time of 10 hours led to significant loss of reduction efficiency. Nitrate was also successfully reduced by in excess of 97% from a 31 mgL^{-1}

influent concentration, with no detected decrease of nitrate reduction efficiency at lower retention times suggesting the two processes are at least partially independent. Batch operation during initial reactor startup was crucial to subsequent successful operation, as lack of any biofilm at commencement of continuous flow conditions led to a propensity for loss of bromate reduction. Backwashing was not essential for efficient operation using an open plastic packing media.

Biological bromate reduction is currently a sparsely studied subject, and contamination of groundwater with bromate is not known as a widespread problem. The current process has the potential for removal of concentrations of bromate higher than those previously investigated for ozonation processes. It has shown that bromate can be remediated from groundwater under pilot-scale conditions using a fixed-film system and glucose as carbon source. Utilisation for remediation of potable water would require significant further optimisation to minimise carbon and biomass residues in treated water. However, this system is envisaged as a tool for source reduction in a bromate-contaminated aquifer using a process of pump, treat and either reinject into the aquifer or pump to sewer. Use in this capacity could provide a simple and cost-effective methodology for gradual source reduction of bromate concentrations within a contaminated aquifer.

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