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WATER QUALITY FACTORS AFFECTING BROMATE REDUCTION IN BIOLOGICALLY ACTIVE CARBON FILTERS

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Abstract—Biological removal of the ozonation by-product, bromate, was demonstrated in biologically active carbon (BAC) filters. For example, with a 20-min EBCT, pH 7.5, and influent dissolved oxygen (DO) and nitrate concentrations 2.1 and 5.1 mg/l, respectively, 40% bromate removal was obtained with a 20 µg/l influent bromate concentration. In this study, DO, nitrate and sulfate concentrations, pH, and type of source water were evaluated for their effect on bromate removal in a BAC filter. Bromate removal decreased as the influent concentrations of DO and nitrate increased, but bromate removal was observed in the presence of measurable effluent concentrations of DO and nitrate. In contrast, bromate removal was not sensitive to the influent sulfate concentration, with only a slight reduction in bromate removal as the influent sulfate concentration was increased from 11.1 to 102.7 mg/l. Bromate reduction was better at lower pH values (6.8 and 7.2) than at higher pH values (7.5 and 8.2), suggesting that it may be possible to reduce bromate formation during ozonation and increase biological bromate reduction through pH control. Biological bromate removal in Lake Michigan water was very poor as compared to that in tapwater from a groundwater source. Bromate removal improved when sufficient organic electron donor was added to remove the nitrate and DO present in the Lake Michigan water, indicating that the poor biodegradability of the natural organic matter may have been limiting bromate removal in that water. Biological bromate removal was demonstrated to be a sustainable process under a variety of water quality conditions, and bromate removal can be improved by controlling key water quality parameters.
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Key words—bromate, disinfection by-product, reduction, granular activated carbon, biologically active carbon

Abbreviations—BAC, biologically active carbon, BrO₃⁻, bromate, CUW, Champaign-Urbana water, DBP, disinfection by-product, DO, dissolved oxygen, DOC, dissolved organic carbon, EBCT, empty bed contact time, EPA, Environmental Protection Agency, GAC, granular activated carbon, LOD, limit of detection, LMW, Lake Michigan water, NH₃, ammonia, NO₃⁻, nitrate, NOM, natural organic matter

NOMENCLATURE

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INTRODUCTION

Ozone has been applied in drinking water treatment as a disinfectant, to oxidize taste and odor compounds and organic micropollutants, and to increase the biodegradability of natural organic matter

(NOM) present in natural water. While the benefits of ozonation are numerous, the production of disinfection by-products (DBPs) must also be considered. After ozonation of water that contained bromide, Richardson *et al.* (1999) observed the formation of dibromoacetonitrile and twenty unhalogenated DBPs previously unreported as ozonation by-products. von Gunten and Hoigné (1994) determined that both molecular ozone and hydroxyl radicals can contribute to the oxidation of bromide to bromate (BrO₃⁻). A survey of nine full-scale drinking water treatment plants and one pilot-scale plant using ozone showed bromate formation in the range of <2–19 µg/l (Lefebvre *et al.*, 1995). Bromate is an especially important ozonation by-product since it has been shown to cause renal cell tumors in rats

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(Kurokawa *et al.*, 1986; DeAngelo *et al.*, 1998) and male mice (DeAngelo *et al.*, 1998) that were fed aqueous bromate. Based on its status as a likely human carcinogen (EPA, 1998a), bromate has been regulated in the United States by the Stage 1 Disinfectants/Disinfection By-Products Rule at 10 µg/l. Under typical risk-assessment conditions (70-kg adult consuming 2 l of water per day for 70 yr), the Environmental Protection Agency (EPA, 1998b) calculated that a 5 µg/l bromate concentration results in a lifetime cancer risk of 10^{-4} .

Abiotic bromate reduction has been achieved in a variety of ways including granular activated carbon (GAC) filtration (Bao *et al.*, 1999; Kirisits *et al.*, 1998; Miller *et al.*, 1996) and semiconductor photocatalysis (Mills *et al.*, 1996). Biological reduction of bromate has also been evaluated. Hijnen *et al.* (1995) isolated denitrifying organisms that were able to reduce bromate with ethanol as the electron donor and carbon source, and Hijnen *et al.* (1999) demonstrated bromate reduction in a denitrifying bioreactor fed with methanol. Biological bromate removal was also observed in a denitrification system that was set up to remove nitrate from a large-scale artificial seawater aquarium (Grguric and Coston, 1998).

Hijnen *et al.* (1999) concluded that biological bromate reduction would not be possible in drinking water treatment systems due to the long contact times required for bromate reduction and the need for extensive post-treatment to remove trace concentrations of external electron donor. However, Kirisits and Snoeyink (1999) observed bromate reduction in natural water from 20 to 10 µg/l by biologically active carbon (BAC) filtration without the addition of an external electron donor and with relatively short contact times, i.e. between 10 and 20 min.

Since denitrifying organisms have been shown to reduce bromate (Hijnen *et al.*, 1995), it is possible that nitrate reductase—the enzyme that catalyzes nitrate reduction—may also catalyze microbial bromate reduction. Barber and Notton (1990) demonstrated that bromate could act as the terminal electron acceptor for reduced nitrate reductase purified from spinach. Nitrate reductase synthesis and activity are generally negatively affected by the dissolved oxygen (DO) concentration. A number of microorganisms have low DO thresholds (<0.5 mg/l) for denitrification (Tiedje, 1988) and do not denitrify until the DO concentration is below the threshold. Consistent with the hypothesis that denitrifiers reduce bromate, Kirisits and Snoeyink (1999) showed that increasing the DO concentration in the influent to a BAC filter negatively impacted bromate reduction. Furthermore, increasing the influent nitrate concentration caused a decrease in bromate removal, suggesting that nitrate and bromate are competing terminal electron acceptors (Kirisits and Snoeyink, 1999).

The primary objective of this research was to evaluate the effect of various water quality para-

meters on biological bromate reduction in a BAC filter, including different source waters and a wide range of influent pH values and concentrations of DO, nitrate, and sulfate.

MATERIALS AND METHODS

Materials

Champaign-Urbana tapwater (CUW; Champaign, IL), which originates from a groundwater source, was dechlorinated by sodium sulfite addition. Raw Lake Michigan water (LMW) was obtained from the crib of the South Water Production Plant (Chicago, IL), located 3.2 km from shore at a depth of 9.6–10.5 m.

Reagent-grade sodium bromate (Aldrich Chemical Co., Inc., Milwaukee, WI) was used to prepare the aqueous anion solution. The lithium salt of DL-lactic acid and the sodium salt of pyruvic acid (Sigma Chemical Co., St. Louis, MO) were used as exogenous electron donors for several experiments with LMW. Sodium bromate was dried overnight at 105°C, and all salts were stored in a desiccator.

Biologically active carbon

Carbon filters were constructed in 2.5-cm inner-diameter glass pipes (Ace Glass, Vineland, NJ) and were capped with teflon and steel endcaps. 14.9 g of GAC were placed in each pipe, and a 2.5-cm layer of 3-mm glass beads was placed above and below the carbon bed to promote uniform flow characteristics and prevent channeling. Peristaltic pumps (Masterflex, Cole-Parmer Instrument Co., Vernon Hills, IL) were used to maintain the appropriate flowrate through the filters, and the empty bed contact time (EBCT) was varied by adjusting the flowrate (10.1–1.6 ml/min for 4–50 min EBCTs). Compressed oxygen or nitrogen was used to sparge the influent water to reach the desired DO concentration, and headspace-free influent containers prevented fluctuations in the influent DO concentration.

Norit RO 0.8 GAC and Norit 830 GAC (Norit Americas Inc., Atlanta, GA) were the media in the BAC filters operated with CUW and LMW, respectively. For the CUW experiments, the GAC was extensively contacted with CUW to exhaust the adsorptive capacity of the carbon and establish a biofilm, as described by Kirisits and Snoeyink (1999). GAC taken from the full-scale plant at the Paul M. Neal Water Treatment Facility (Lake Bluff, IL) was used for the LMW experiments. This carbon had been used for approximately 7 yr to treat ozonated LMW. Prior to packing the carbon into the column, the BAC was rinsed with deionized-distilled water to remove excessive turbidity. Since this carbon was already biologically active, no extensive preloading period was required.

A schematic diagram of the experimental apparatus is shown in Fig. 1. Two BAC filters were operated in series so that two EBCTs could be evaluated simultaneously. CUW was used in the experiments to investigate the effects of DO, nitrate, and sulfate concentrations and pH on bromate removal. No exogenous electron donor was added to CUW experiments. For some of the LMW experiments, a syringe pump (74900 series, Cole Parmer Instrument Co., Vernon Hills, IL) was used to add an electron donor solution containing 1.2 mM pyruvic acid (10 electron equivalents/mol¹) and 1.0 mM lactic acid (12 electron equivalents/mol). The relative flow rates between the peristaltic pump and the syringe pump (Fig. 1) determined the influent dissolved

¹The number of electron equivalents per mole was calculated assuming mineralization of the organic acid to carbon dioxide.

organic carbon (DOC) concentration in each experiment. The final influent DOC concentrations for these experiments were measured just prior to the inlet of the first column, and they are shown in Table 3.

Sampling

Each experimental condition was maintained for at least two days prior to the first sampling event. Thereafter, sampling continued for at least ten days but usually for more than two weeks. If the percent bromate removal steadily increased or decreased over time, these data were not used to calculate the average percent bromate removal for the experiment; instead, the experiment was extended until steady state was achieved, and these data were used to calculate the average bromate removal. Steady state was defined as seven or more consecutive bromate removal data points within the 95% confidence limits of the average. Since average percent bromate removals were not needed for LMW experiments, these experiments were not always run long enough to achieve steady state with respect to bromate removal.

In summary, the average bromate removal for each water quality condition was calculated based on multiple sampling events (7–23 samples) over a time period greater than ten days. To determine if the difference in bromate removal between two experiments was statistically significant, the Student's *t*-test was applied at the 95% confidence interval.

Analytical methods

Bromate, nitrite, nitrate, and sulfate concentrations were determined using a Dionex Series 300 ion chromatograph (Sunnyvale, CA) with an anion self-regenerating suppressor (ASRS-1) and conductivity meter. Three Dionex Ionpac columns were used in series—NG1, AG9-HC, and AS9-HC. The NG1 guard column was used to adsorb organic material that could potentially foul the analytical column. The analytical method included a 9.0 mM sodium carbonate eluant, 1.0 ml/min flowrate, and 250 μ l injection loop.

The limit of detection (LOD) for bromate was calculated to be approximately 2 μ g/l. Clarke (1998) showed that concentrations below the LOD could be handled by recording them as one half of the LOD, and this method was as good or better than more complicated methods. Therefore, any bromate concentration that was less than 2 μ g/l was recorded as 1 μ g/l.

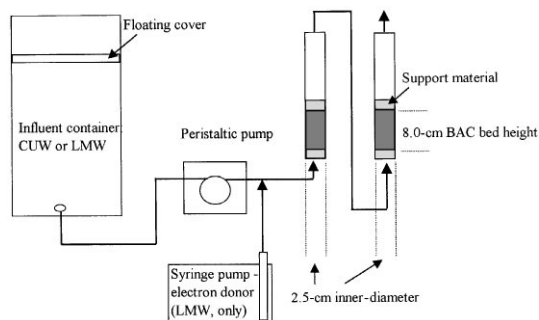


Fig. 1. Schematic of BAC filtration experiments.

A YSI Model 58 DO meter with a 5905 probe (Yellow Springs, OH) was used to measure DO. An Orion 720A pH/Ion Selective Electrode Meter with an Orion ammonia probe 95-12 (Beverly, MA) was used to determine ammonia concentrations. Samples for DOC analysis were filtered through 0.45- μ m nylon membranes and were analyzed by UV-persulfate oxidation with a Phoenix 8000 TOC Analyzer (Tekmar-Dohrmann, Cincinnati, OH). The TOC analyzer, calibrated with potassium hydrogen phthalate standards, measured organic carbon after first pretreating the samples to remove inorganic carbon.

RESULTS AND DISCUSSION

General operating conditions and water characteristics

The BAC filtration experiments were run with two filters in series (Fig. 1). External electron donor was only added to some of the LMW experiments (Fig. 1). The BAC filters were typically operated with an influent DO concentration of 2 mg/l, pH 7.5, and background concentrations of nitrate and sulfate. These conditions were systematically varied, one at a time, to assess the effect of each parameter on bromate removal in the BAC filters.

Average water characteristics of CUW and LMW are listed in Table 1. The main differences between the two waters were the ammonia (NH₃) concentrations and biodegradability of the organic matter. CUW contained less than 1.70 mg/l NH₃-N, with an average concentration of 0.80 mg/l, and the NH₃-N concentration in LMW was below the detection limit of 0.05 mg/l. The organic matter in CUW displayed some degree of biodegradability in the BAC filter, with an average DOC removal of 25%. The organic matter in LMW was fairly inert in the BAC filter with an average DOC removal of 4%.

Effect of dissolved oxygen

To evaluate the effect of DO concentration on bromate removal, the BAC filters were operated with CUW with varying DO concentrations (Table 2). The influent nitrate concentration was relatively constant for all experiments (between 4.6 and 5.3 mg/l), although the nitrate concentration in the filters increased due to nitrification of the ammonia present in the influent (Table 2). The data in Table 2 show that the effluent DO concentration was below the detection limit (0.1 mg/l) when the influent DO concentration was \leq 5.8 mg/l. When the influent DO concentration was raised to 8.0 mg/l and higher, the effluent DO concentration was above the detection limit.

Table 1. Average water characteristics of CUW and LMW with 95% confidence limits

Water	Nitrate (mg/l)	Sulfate (mg/l)	DOC (mg/l)	Ammonia (mg/l as N)
CUW	0.35 \pm 0.04	1.0 \pm 0.2	1.4 \pm 0.1	0.80 \pm 0.14
LMW	1.64 \pm 0.06	23.0 \pm 0.4	2.4 \pm 0.2	< 0.05

Table 2. Effect of influent DO concentration on bromate removal in BAC filters (Average influent conditions: CUW, pH 7.5, 20 µg/l bromate)

Expt.	EBCT (min)	Average DO concentration (mg/l)		Average nitrate concentration (mg/l)		Average nitrate production (mg/l as N)		Average ammonia concentration (mg/l as N)		Average ammonia consumption (mg/l as N)		Average bromate removal with 95% confidence limits (%)
		Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
1	10	2.1	<0.1	5.3	6.2	0.2	0.7	0.4	0.3	2.3 (±4)		
	20		<0.1		7.7	0.6		0.3	0.4	40 (±5)		
2	10	3.8	<0.1	5.1	8.0	0.7	1.0	0.2	0.8	12 (±5)		
	20		<0.1		8.6	0.8		0.0	0.9	25 (±6)		
3	10	5.8	<0.1	4.6	7.7	0.7	0.8	0.1	0.7	9 (±4)		
	21		<0.1		7.9	0.8		0.1	0.7	19 (±4)		
4	10	8.0	1.8	5.0	9.0	0.9	0.8	0.0	0.8	9 (±4)		
	21		0.8		8.9	0.9		0.0	0.8	14 (±5)		
5	10	13.6	7.5	5.0	9.7	1.1	NA ^a	NA	NA	4 (±9)		
	21		5.1		9.7	1.1		NA	NA	11 (±9)		

^a No data available.

There was a statistically significant decrease in bromate removal, at the 95% confidence level, as the influent DO concentration was increased from 2.1 to 3.8 mg/l (Table 2). This was expected since oxygen, a common electron acceptor, may inhibit the expression or activity of the enzymes required for bromate reduction. Additionally, the increased DO concentration could cause more competition for electron donor. Although effluent DOC concentrations were usually greater than 0.7 mg/l, the presence of residual DOC provides no indication of the ability of the bromate-reducing organisms to use this DOC. Thus, it can be hypothesized that the appropriate substrates for bromate-reducing organisms had been consumed by aerobic organisms and were therefore not available for additional bromate reduction. To validate this hypothesis, it would be necessary to monitor the consumption of compounds that can serve as electron donors for bromate reduction under various DO conditions.

As the influent DO concentration was increased from 3.8 to 13.6 mg/l, the average percent bromate removals were no longer statistically different at the 95% confidence level (Table 2). Thus, the same bromate removal was obtained if the filter influent contained a DO concentration of 3.8 or 13.6 mg/l.

The average percent bromate removal observed in the experiment with an influent DO concentration of 13.6 mg/l was only 11% after a 21-min EBCT (Table 2). Even though nitrification and aerobic respiration consumed 8.5 mg/l DO during the 21-min EBCT, the remaining DO (> 5.1 mg/l throughout the filter) prevented much bromate removal. As mentioned before, bromate removal may also have been prevented by electron donor limitation due to electron donor consumption by aerobic respiration. Therefore, it is likely that full-scale ozone-BAC plants are not observing biological bromate reduction in their BAC filters because the DO concentration is too high. Treatment systems that generate ozone from pure oxygen may have influent DO concentrations greater than 10 mg/l. For example, in the full-scale post-ozonation BAC filters at the Paul M. Neal Water Treatment Facility (Lake Bluff, IL), bromate is not reduced from the 6 µg/l influent concentration after a 15-min EBCT (Soucie, 1999); this is likely due to the fact that the average influent and effluent DO concentrations are 11.5 and 10.7 mg/l, respectively. Based on this information, it is doubtful that extended acclimation of the bench-scale BAC filters to high DO concentrations would have improved bromate removal by selecting for bromate reducers with greater oxygen tolerance.

Aforementioned, the expression and activity of the enzymes required for denitrification are often affected by the DO concentration (Tiedje, 1988). While denitrification is primarily thought of as an anoxic process, denitrification has also been observed under aerobic conditions (Robertson and Kuenen, 1984). In *Thiosphaera pantotropa* (now *Paracoccus*

denitrificans, Ludwig *et al.*, 1993), Bell *et al.* (1990) found that the nitrate reductases involved under aerobic conditions are different from those used under anaerobic conditions. A membrane-bound nitrate reductase is primarily expressed under anaerobic conditions; a periplasmic nitrate reductase is primarily expressed under aerobic conditions but is active under aerobic and anaerobic conditions. Ye *et al.* (1994) noted that aerobic denitrifiers, such as *Paracoccus denitrificans*, are rare organisms. However, Lloyd *et al.* (1987) demonstrated aerobic denitrification with eight bacterial isolates and concluded that aerobic denitrification may be common in the environment. Bell *et al.* (1990) observed that the aerobic rate of nitrate reduction was approximately one-tenth of the anaerobic rate of nitrate reduction; thus, the lower rate of aerobic denitrification may make aerobic denitrifiers more difficult to identify. It is possible that aerobic denitrifiers are present in the BAC filters used in the current study since bromate reduction was observed in the presence of DO for 36 days (Experiments 4 and 5, Table 2). The low percent bromate removal observed under aerobic conditions would be consistent with the slow rate of aerobic denitrification observed by Bell *et al.* (1990). Additionally, even in an aerobic filter, it is possible that anoxic microniches are created where bromate reduction can take place without inhibition by oxygen.

The effluent nitrate concentration increased as the influent DO concentration increased due to biological nitrification (Table 2). However, in Experiments 4 and 5, the average effluent nitrate concentration from the 21-min EBCT filter was the same as or close to the effluent nitrate concentration from the 10-min EBCT filter. This indicates that all of the nitrification took place in the first (10-min EBCT) filter for these experiments.

In general, the measured DO consumption (Table 2) was greater than the calculated consumption of DO required for the observed nitrate production. This indicates that some of the DO was also used in aerobic respiration. Also, the amount of ammonia consumed in the BAC filters was close to the amount of nitrate produced; generally the two values were within 0.1 mg/l as N (Table 2).

There is no evidence that significant denitrification took place in the filters, since influent and effluent nitrogen levels (ammonia, nitrite, and nitrate) were similar (data not shown). Based on the results of Hijnen *et al.* (1999), one might expect a faster rate of nitrate reduction as compared to bromate reduction since the nitrate concentration was two orders of magnitude greater than the bromate concentration in the BAC filters. Due to the low concentration of biodegradable organic matter in drinking water, it is likely that microbial activity—including denitrification—was limited by the electron donor concentration. Additionally, a low concentration of electron

donor can result in measurable effluent DO (Experiments 4 and 5, Table 2), which can also inhibit the enzymes required for denitrification. These points are illustrated in a later section where significant nitrate removal is observed upon addition of an external electron donor to a drinking water source.

Effect of nitrate

Kirisits and Snoeyink (1999) showed a decrease in bromate removal as the influent nitrate concentration was increased over a relatively narrow concentration range (0.3–5.0 mg/l). Figure 2 expands this result to show how bromate removal decreased as the influent nitrate concentration was increased from 0.3 to 42.3 mg/l. With a 26-min EBCT, bromate removal dropped from 86 to 49% as the influent nitrate concentration increased from 0.3 to 42.3 mg/l (Fig. 2(a)). With a 51-min EBCT, bromate removal decreased only from 95 to 79% for the same increase in nitrate concentration (Fig. 2(b)). Thus, the 51-min EBCT seemed to dampen the negative effect of an increased nitrate concentration.

Two data points in each of Fig. 2(a) and (b) are denoted as outliers (influent nitrate concentrations of 10.9 and 32.1 mg/l). These experiments were run with a different set of BAC filters than the rest of the experiments shown in Figs. 2(a) and (b). A timeline, showing the history of these filters, is shown in Fig. 2(c). Figure 2(c) shows that the filters were exposed

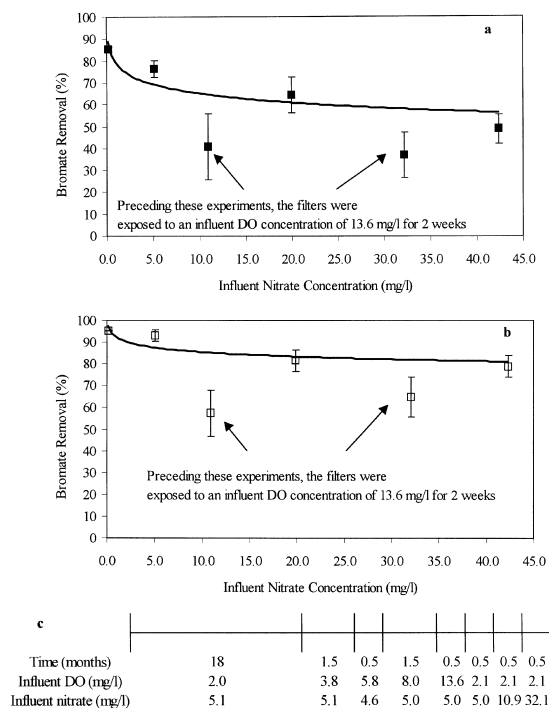


Fig. 2. Effect of influent nitrate concentration on bromate removal in BAC filters (Average influent conditions: CUW, pH 7.5, 20 µg/l bromate, 4.0 mg/l sulfate, 2.1 mg/l DO). (a) 26-min EBCT; (b) 51-min EBCT; (c) BAC filter timeline.

to influent DO concentrations between 3.8 and 8.0 mg/l for 3.5 months and 13.6 mg/l for two weeks prior to reducing the influent DO concentration to 2.1 mg/l. It is likely that filter history had an effect on subsequent experiments, since these data points are significantly below the curve fitted through the other data in Fig. 2(a) and (b). The negative effect of higher DO concentrations on the bromate-reducing bacteria was not reversible. Even after the filters had been operated with an influent DO concentration of 2 mg/l for four months beyond the end of the timeline in Fig. 2(c), they showed no indication of regaining their original bromate reduction capability. Thus, it seemed that a new steady state had been established in these columns.

The above data suggest that it may be necessary to monitor the DO concentration of the backwash water. However, the effects of short-term high DO concentrations on biological bromate removal have not yet been assessed; the effect on bromate removal would likely depend on the frequency and duration of backwash. Simpkin and Boyle (1988) found that nitrate and nitrite reductases were synthesized to at least 50% of their maximum levels in activated sludge systems operated with aerobic and anoxic cycles; they concluded that the repression of nitrate reductase and nitrite reductase synthesis by oxygen was not as important as the effect of oxygen on the enzyme activities. Thus, if nitrate reductase is involved in bromate reduction, it is possible that a short backwash, with DO in the backwash water, would not affect bromate removal. However, the current study showed that operation of the BAC filters with influent DO concentrations between 3.8 and 13.6 mg/l for four months resulted in poorer bromate removal in subsequent experiments. Since filter history can have a significant effect on bromate removal, it is important that bromate removal comparisons be made only between filters that have similar histories. The reader is cautioned against data comparisons *between* tables or figures in this paper unless it is specifically stated that the BAC filter histories are similar.

Effect of sulfate

Sulfate can serve as an electron acceptor for sulfate-reducing bacteria. In contrast to bromate, nitrate, and DO—which are high potential terminal electron acceptors ($E_{\text{BrO}_3^-/\text{Br}^-}^{\circ} = 1.03 \text{ V}$; $E_{\text{O}_2/\text{H}_2\text{O}}^{\circ} = 0.82 \text{ V}$; $E_{\text{NO}_3^-/\text{NO}_2^-}^{\circ} = 0.43 \text{ V}$)—sulfate is a low potential terminal electron acceptor ($E_{\text{SO}_4^{2-}/\text{HS}^-}^{\circ} = -0.22 \text{ V}$). Thus, sulfate reduction generally takes place after bromate, nitrate, and DO have been depleted. Based on this, the sulfate concentration was not expected to have a considerable impact on bromate reduction in the BAC filter. To test this hypothesis, the effect of sulfate concentration on bromate reduction in a BAC filter was evaluated with influent sulfate concentrations between 11.1 and

102.7 mg/l. Sulfate reduction did not take place in any of the experiments, since the influent and effluent sulfate concentrations were equal (Fig. 3). As the sulfate concentration increased, the average percent bromate removal declined just slightly in the BAC filters with 25- and 50-min EBCTs (Fig. 3). This is similar to the findings of Chen and Hao (1996), who observed that 120 mg/l sulfate slightly inhibited microbial chromate reduction even though no sulfate reduction was observed.

Effect of pH

It is useful to evaluate the sensitivity of bromate-reducing microorganisms to pH changes, so that conditions for biological bromate reduction can be optimized. To assess the effect of pH on bromate reduction, four BAC filtration experiments were run with pH values of 6.8, 7.2, 7.5, and 8.2. The system was well-buffered, and the effluent pH values deviated from the influent values by less than 0.1 pH units. Bromate removal generally decreased as the influent pH increased from 6.8 to 8.2 (Fig. 4). The percent bromate removals observed at pH values of 6.8 and 7.2 are not different at the 95% confidence level, which might indicate that the optimum pH for bromate removal is in this region. Since bromate formation during ozonation is also dependent on the pH, bromate formation could be reduced and

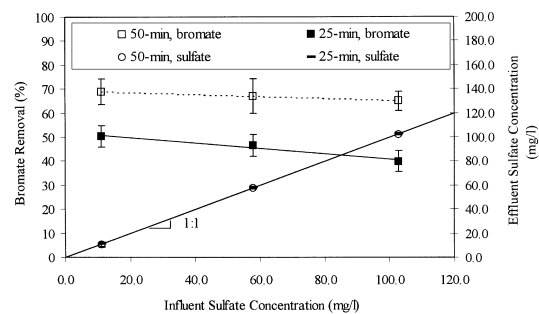


Fig. 3. Effect of influent sulfate concentration on bromate removal in BAC filters (Average influent conditions: CUW, pH 7.5, 21 $\mu\text{g/l}$ bromate, 2.1 mg/l DO, 0.3 mg/l nitrate).

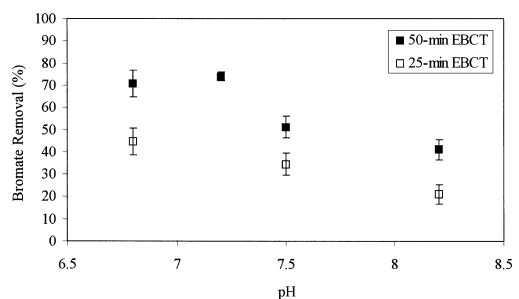


Fig. 4. Effect of influent pH on bromate removal in BAC filters (Average influent conditions: CUW, 20 $\mu\text{g/l}$ bromate, 2.1 mg/l DO, 5.0 mg/l nitrate).

biological bromate reduction could be increased by pH control. For example, Song *et al.* (1996) observed a 50% reduction in bromate formation by reducing the pH from 8.0 to 7.0. Thus, if the pH for ozonation were decreased to the near-neutral range (6.8–7.2) to reduce bromate formation, the data presented in Fig. 4 show that biological bromate removal would also be improved. Although pH 6.8 and 7.2 yielded the highest percent bromate removal, the true optimum pH can only be found by evaluating a narrower range of pH values since biological reduction rates can be very sensitive to small changes in pH. For instance, Chen and Hao (1996) observed a doubling in the initial specific microbial chromate reduction rate as the pH increased from 7.0 to 7.3.

Effect of source water

To evaluate if the type of source water would have an effect on bromate reduction, experiments were run with raw water from Lake Michigan using 7-yr old BAC from the Paul M. Neal Water Treatment Facility (Lake Bluff, IL). Since this plant treats water from Lake Michigan, it was appropriate to use this BAC for the LMW experiments. The influent DO concentration was approximately 2 mg/l, and the pH was 7.5. Table 3 shows pertinent experimental information. The LMW experiment was separated into five experimental phases—A through E. Each phase had a different electron donor dose and/or EBCT. Table 3 shows the concentrations of exogenous electron donor and total DOC. The total influent DOC concentration is the sum of the organic matter present in LMW (2.4 mg C/l) and the concentration of exogenous electron donor. Fig. 5(a) and (b) show bromate and nitrate removal for each phase of the experiment.

At the beginning of the experiment (Phase A), no external electron donor was added to the influent. Table 3 shows that little DOC removal was observed in Phase A in the 15-min EBCT BAC filters, indicating the presence of little biodegradable organic matter in LMW. In the full-scale plant from which the BAC was obtained, an average of 20% DOC removal from LMW was observed in a 15-min EBCT filter (Soucie, 1999). The difference in DOC removal between the bench- and full-scale BAC filters was likely due to the fact that the bench-scale influent was not ozonated while the full-scale filter receives ozonated influent (0.1 mg ozone/mg DOC). Very little bromate removal was observed in Phase A (Fig. 5(a)). Fig. 5(b) shows that only a small amount of nitrate was produced in the BAC filter (negative nitrate removal) because the influent $\text{NH}_3\text{-N}$ concentration was routinely below the detection limit of 0.05 mg/l. The effluent DO concentration was 0.8 mg/l (Table 3), which indicates the presence of biological activity in the filter. By comparison, Kirisits and Snoeyink (1999) showed that an 18-min EBCT BAC filter using CUW under similar conditions (pH 7.5,

Table 3. DOC removal and DO remaining in BAC experiments using LMW (Average influent conditions: LMW, 2.0 mg/l DO, pH 7.5, 21 $\mu\text{g/l}$ bromate, 1.6 mg/l nitrate)

Phase	EBCT (min)	Exogenous electron donor: lactate + pyruvate (mg C/l)	Total DOC concentration (mg/l)		DOC removal (%)	Effluent DO concentration (mg/l)
			Influent	Effluent		
A	15	0	2.4	2.3	4	0.8
B	15	1.0	3.4	2.3	34	0.2
C	30	3.1	5.5	2.0	63	0.2
D	15	3.6	6.0	2.6	57	0.2
E	15	0.6	3.0	1.9	37	0.2

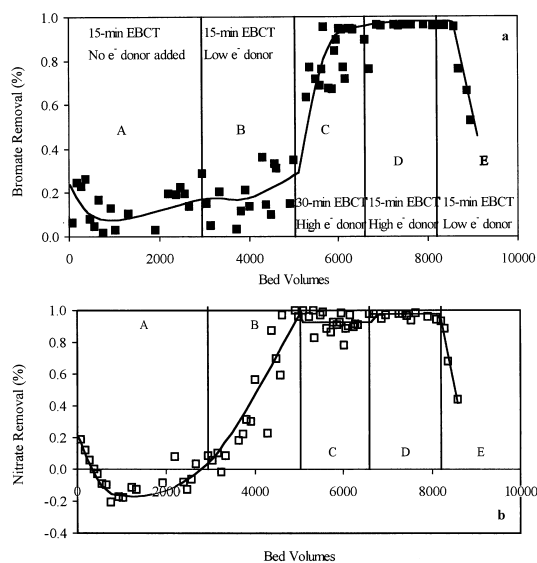


Fig. 5. (a) Bromate removed in the BAC filter with LMW; (b) nitrate removed in the BAC filter with LMW. (Average influent conditions: LMW, 2.0 mg/l DO, pH 7.5, 21 μ g/l bromate, 1.6 mg/l nitrate).

influent DO = 2.0 mg/l, effluent DO = 0.2 mg/l, influent nitrate = 0.3 mg/l, effluent nitrate = 2.1 mg/l, influent bromate = 20 μ g/l) removed 71% of the bromate. It is notable that the BAC filter treating CUW reduced the influent $\text{NH}_3\text{-N}$ concentration from 0.8 to 0.6 mg/l and the influent DOC concentration from 1.3 to 0.9 mg/l. DO removal through ammonia consumption (0.2 mg/l as N) and the presence of 0.4 mg/l DOC for biodegradation provided favorable conditions for bromate removal in CUW. The reduction of bromate in LMW was likely hindered by a combination of factors which are explained as follows. Only a small amount of DO was consumed in the biological nitrification reaction because of the low ammonia concentration in LMW. The presence of DO resulted in the consumption of biodegradable organic matter, leaving less electron donor available for bromate reduction. Additionally, since only 0.1 mg/l DOC was removed from LMW in the BAC filter (Table 3), the concentration of biodegradable organic matter in LMW was likely quite low. Alternatively, if nitrate reductase catalyzes bromate reduction, the DO could also have inhibited its synthesis or activity.

Lactate and pyruvate (1.0 mg C/l) were added to the influent in Phase B, and the EBCT was maintained at 15 min. There was not much difference in the amount of bromate removed between Phases A and B (Fig. 5(a)), despite the fact that significant DOC removal was observed in Phase B (Table 3). The low effluent DO concentration (0.2 mg/l) suggests that much of the DOC in Phase B was being used by aerobic microorganisms. Since nitrate removal became significant in Phase B (Fig. 5(b)),

DOC was also being consumed by nitrate reducers. This may indicate that a nitrate-reducing population was developing on the carbon but that this population was not able to reduce bromate due to an insufficient concentration of electron donor.

In Phase C, the EBCT in the BAC filter was doubled from 15 to 30 min, and the external electron donor concentration was increased to 3.1 mg C/l (Table 3) to provide a favorable environment for bromate reduction. Bromate removal increased until the effluent bromate concentration reached the detection limit (Fig. 5(a)), while nitrate removal was sustained (Fig. 5(b)).

When the EBCT was reduced from 30 to 15 min (Phase D) while the external electron donor concentration was maintained close to the concentration in Phase C (Table 3), complete bromate removal was sustained (Fig. 5(a)), and nitrate removal remained efficient (Fig. 5(b)). This shows that the electron donor concentration, and not the EBCT, was limiting bromate removal in these experiments. This is different from the results observed in experiments with CUW which had shown that bromate removal increased as the EBCT increased indicating that EBCT was limiting bromate removal (Table 2 and Figs 2-4).

The effluent DOC concentration in Phase D (2.6 mg/l) was greater than that for any of the other phases, indicating that some of the exogenous electron donor had not been mineralized. This is likely attributable to the fact that a high exogenous electron donor concentration was used in Phase D (3.6 mg/l) for a 15-min EBCT filter. Thus, the EBCT should be lengthened or the concentration of exogenous electron donor reduced so that residual electron donor would not be present to encourage regrowth in the distribution system.

Finally, the external electron donor concentration was decreased to 0.6 mg C/l while maintaining an EBCT of 15 min in Phase E (Table 3). Fig. 5(a) and (b) show that bromate and nitrate removal began to decrease. It is likely that the electron donor concentration was limiting the growth of nitrate- and bromate-reducing organisms. With less electron donor present, there was a decreased demand for nitrate and bromate as electron acceptors.

Based on the results of the LMW experiments, it can be concluded that the biodegradability of the NOM in the source water can significantly affect biological bromate removal. Ozonating the LMW to increase the biodegradable fraction of NOM may improve bromate removal.

CONCLUSIONS

BAC filters were able to reduce bromate under a variety of water quality conditions. Water quality parameters affecting microbial physiology and growth will affect the efficiency of bromate removal.

Based on the data collected in this study, the following conclusions were drawn:

- Increasing the concentration of influent DO caused a decrease in bromate removal. The lack of bromate reduction observed in full-scale ozone-BAC plants is likely due to the high concentrations of DO entering the filters.
- Increasing the influent nitrate concentration caused a decrease in bromate removal. Nitrate and bromate may be competing terminal electron acceptors.
- The negative effect of higher DO concentrations on the bromate-reducing bacteria persisted even after the influent DO concentration was reduced. A BAC filter, which had previously been exposed to influent DO concentrations between 3.8 and 13.6 mg/l for four months, yielded significantly lower bromate removal efficiency than expected when it was operated with an influent DO concentration of 2.0 mg/l for one month.
- Increasing the concentration of sulfate from 11.1 to 102.7 mg/l only caused a slight decline in bromate removal for the BAC filters. No significant sulfate reduction was detected in the filters.
- Bromate removal increased as the influent pH decreased from 8.2 to the near-neutral range of 6.8–7.2. It may be possible to reduce bromate formation during ozonation and increase biological bromate removal through pH control since bromate formation decreases as the pH is reduced.
- Under similar operating conditions, bromate removal in an 18-min EBCT BAC filter using CUW (a groundwater source) was much higher than bromate removal obtained in a 15-min EBCT BAC filter using LMW. Ammonia consumption reduced the DO concentration in the CUW experiment, but little ammonia was available in the LMW for DO reduction. Also, 0.4 mg/l DOC was biodegraded in CUW whereas only 0.1 mg/l DOC was biodegraded in LMW. Therefore, bromate-reducing microorganisms in LMW may have been inhibited by residual DO and limited by the electron donor concentration.
- Only one BAC filtration experiment using LMW amended with exogenous electron donor yielded an effluent DOC concentration (2.6 mg/l) in excess of the concentration of NOM present in LMW (2.4 mg/l). Thus, if the addition of exogenous electron donor were being considered in conjunction with BAC filtration for bromate removal, the residual electron donor concentration would have to be monitored to prevent regrowth problems in the distribution system.

While filtration experiments provide insight into how bromate removal can be affected by various water quality conditions, isolation of bromate-redu-

cing microorganisms from the BAC filters will be key in further understanding biological bromate reduction. Identification and characterization of specific bromate-reducing microorganisms may aid in optimizing conditions for bromate reduction in the BAC filters.

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