Adsorption/reduction of bromate from drinking water using GAC: Effects on carbon characteristics and long-term pilot study

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Abstract

This study investigated the feasibility of using granular activated carbon (GAC) to remove bromate (BrO_3^-) from drinking water through batch experiments, rapid small-scale column tests (RSSCT) and a pilot-scale study. The results indicated that the GAC capacity for BrO_3^- removal was dependent on the GAC surface characteristics and empty-bed contact time (EBCT). The GAC with a high number of basic groups and higher pH_{pzc} values showed an increased BrO_3^- removal capacity. On the other hand, BrO_3^- removal was improved by increasing EBCT. In the GAC pilot plant, a GAC column (operating with 15 min EBCT) preload for 12 months achieved a BrO_3^- and assimilable organic carbon (AOC) removal rate ranging between 7 and 96 % and between 41 and 85 %, respectively. The amount of BrO_3^- removed was found to be proportional to the influent BrO_3^- concentration. Based on the results of our long-term experiment, the BrO_3^- and AOC removal rate during the transition from initial GAC to biological activated carbon (BAC) was calculated as 0.12 % w/w and 0.27 % w/w, respectively. However, the BrO_3^- removal rate apparently decreased with increasing operating time (after 3 months). This may be a result of the contribution of the bacterial biomass being adsorbed on the GAC surface which hindered BrO_3^- reduction by GAC, either by blocking the pores or adsorbing on the activated sites for BrO_3^- reduction.

Keywords: granular activated carbon, biological activated carbon, bromate, assimilable organic carbon

Introduction

Bromate (BrO_3^-) is a genotoxic carcinogen (Kurokawa et al., 1986) which may be present in drinking water when ozonation is applied in the treatment of bromide-containing water (Haag and Hoigne, 1983). Concentrations of 5 to 10 mg/ℓ have been observed after treatment in full-scale drinking water production plants (Krasner et al., 1993). The bromate concentration in drinking water corresponding with a cancer risk of 10^{-5} (life-time exposure) is 3 µg/ℓ (WHO, 1993). The USEPA criteria document for ozone and its by-products used the linearised multistage model to estimate 10^{-6}, 10^{-5}, and 10^{-4} life-time excess cancer risks of 0.05, 0.5, and 5 µg/ℓ bromate, respectively.

Furthermore, ozonation of drinking water transforms natural organic matter (NOM) into a more biodegradable form. This can cause significant bacterial regrowth in the distribution system if biodegradable organic matter (BOM) is not removed by subsequent treatment steps (Van der Kooij and Hijnen, 1984). The concentration of BOM, expressed in terms of assimilable organic carbon (AOC) or biodegradable dissolved organic carbon (BDOC), increases with increasing ozone dosage (Van der Kooij et al., 1982; Servais et al., 1989).

For the removal of BrO_3^- several techniques have been investigated. Batch-scale experiments have shown that BrO_3^- can be reduced to Br^- by ultraviolet irradiation, high energy electron beam irradiation and heterogeneous redox catalysis (Siddiqui et al., 1994; Mills and Meadows, 1995), but the practical performance of these techniques to remove BrO_3^- from ozonated waters appears uneconomical at present. Through jar-test experiments, Siddiqui et al. (1994) reported that the reduction of BrO_3^- to Br^- by the addition of ferrous iron as a reducing agent was feasible if the coagulation process followed ozonation treatment. Several studies have investigated the use of activated carbon (granular or powder) filtration for removing BrO_3^- from water reporting poor to effective BrO_3^- removal. Through bench-and pilot-scale column testing, BrO_3^- could be effectively removed by virgin GAC, but the GAC capacity was found to be carbon-specific and dependent on source waters (Gerz and Schneider, 1993; Siddiqui et al., 1996).

GAC in actual water treatment processes naturally breeds a bacterial population on its surface, and eventually it functions as biological activated carbon (BAC). With the help of the bioactivity on BAC, the reduction of total organic carbon (TOC) and other biodegradable organic matter is considered to maintain a longer service time before GAC regeneration. The combination of ozonation and biological treatment with BAC enhances the degradation removal of organic substances, although it only slightly degrades trihalomethane precursors and aldehydes (Cipparone et al., 1997). On the other hand, there have been some reports of BrO_3^- reduction by BAC (Asami et al., 1999), but results obtained from surveys of various European water utilities have shown low efficiency of GAC for BrO_3^- removal in full-scale plants (Lefebvre, 1995; Legube, 1996).

At present, the number of reports on activated carbon adsorption and removal of ozonation by-products, especially on BAC, are limited. It would be desirable to use GAC for BrO_3^- and AOC removal, since GAC is already in use at many drinking water treatment plants. This study deals with the behaviour of BrO_3^- and AOC in a GAC/BAC filter. The effect of carbon type, EBCT and influent concentration on BrO_3^- removal by activated carbon was assessed.

Materials and methods

Water source

Raw groundwater samples were collected from the Mid-Western part of Taiwan, which is affected by salt-water intrusion. Historically, bromide in this source water has been as high as 1.07 mg/ℓ. Dissolved organic carbon (DOC) was 2.9 mg/ℓ, which was not particularly high, its organic content was found to consist predominantly of hydrophobic organics (including humic acid and fulvic acid). The other characteristics of the water sources studied during this research are summarised in Table 1.

Granular activated carbon (GAC)

Five types of GAC with different origins were evaluated with batch experiments, RSSCT, and pilot-plant experiments for removing BrO_3^- and AOC. The main characteristics of selected GACs (Table 2), such as raw material, mean particle size, total surface area, iodine number, hardness, abrasion, bulk density, and ash content are provided by the manufactures. Acid and basic groups were determined by the acid-base titration procedure described by Siddiqui et al. (1996). The GACs for the batch and RSSCT experiments were prepared by the following procedures: Commercial GACs were pulverised and sieved to obtain 60 x 80 mesh particle sizes, resulting in an average particle diameter of 0.212mm. After sieving, the carbons were washed with deionised water, and dried at 175°C for 1 week to remove volatile impurities, and were then kept in the oven at 105°C. Before use, the carbons were placed in a desiccator and allowed to cool to room temperature. Furthermore, selected activated carbons were washed with 6N HNO_3 by agitating for 24h to investigate enhanced BrO_3^- removal. These carbons were washed thoroughly after acid-washing with organic-free water and dried at 175°C for 1 week.

Batch experiments

BrO_3^- removal experiments using activated carbon (60×80 mesh) were performed by the batch shaker test. The appropriate carbon dose was introduced into 100 mℓ amber glass bottles. The bottles were put on a shaker table for a specified time and filtered through pre-washed 0.45 μm filters.

RSSCT experiments

RSSCT experiments were conducted to evaluate the capacity of GACs for the removal of BrO_3^-. The designed RSSCT test was based on the scaling approach developed by Crittenden et al. (1986) to simulate the performance of a pilot-scale GAC filter described later. RSSCT experiments were performed using 12 mm I.D. glass columns packed with 5 to 6 g of 60 x 80 mesh size of prepared GACs. The GAC bed was 125 mm long. Each side of the GAC bed was packed with 2 mm glass beads with comparable particle size to eliminate entrance and exit flow disturbances.

TABLE 1
Characteristics of water sources

Parameters	Range
pH	7.4~7.6
Alkalinity (mg/ℓ as $CaCO_3$)	105~121
Turbidity (NTU)	<1
Conductivity (μs/cm)	547~936
Bromide (mg/ℓ)	0.72~1.07
Chloride (mg/ℓ)	17.3~23.6
Ammonia-nitrogen (mg/ℓ)	<0.02
Dissolved organic carbon (mg/ℓ)[a]	1.5~1.9
Hydrophobic fraction (mg/ℓ)	0.4~0.7
Hydrophilic fraction (mg/ℓ)	1.0~1.4
AOC (μg acetate-C/ℓ)	52~77
AOC_{P17} (μg acetate-C/ℓ)	33~61
AOC_{NOX} (μg acetate-C/ℓ)	12~28

[a] Dissolved organic carbon classified into hydrophobic and hydrophilic fractions

TABLE 2
Manufacturers' specifications of GACs used

Specifications	F-400[c]	F-820[c]	G-840[d]	Norit[e]	YUB[f]
Material	Bituminous coal	Bituminous coal	Cocount shell	Cocount shell	Torbanite
Mean particle size (mm)	1.2	1.2	1.3	1.4	1.2
Total surface area (m²/g)	950	850	>.1000	950	>.1050
Iodine number (mg/g)	1000	900	>.1050	1020	>.1000
Hardness (Ball-Pan,%.min)	95	95	>.98%	95	>.98%
Abrasion number (%wt.min)	75	75	>.95	0	94
Bulk density (g/mℓ)	0.36~0.38	0.45~0.46	0.31~0.34	0.49~0.52	0.44~0.48
Ash content (%)	6.0	6.0	7.5	< 3 %	< 3 %
Acid groups[a] (meq/g C)	0.38	0.39	0.28	0.21	0.18
Basic groups[a] (meq/g C)	0.23	0.27	0.48	0.57	0.71
Carboxyl groups[a] (meq/g C)	0.16	0.16	0.13	0.10	0.07
pH_{pzc}[b]	6.2	6.1	7.0	7.3	8.0

[a] Acid and basic groups were determined by the acid-base titration procedure described by Siddiquietal (1996)[b] pH of isoelectric points (pHpzc) was determined by surface titration method described [c] Calgon Corp., Pittsburgh, PA[d] China Carbon Corp., Taipei, Taiwan, ROC.[e] Norit, Amersfoort, The Netherlands.[f] Haycarb, Colombo, Sri Lanka.

Water samples with 80 µg/ℓ of BrO$_3^-$ were slowly pumped from a 120 ℓ plastic tank using a peristaltic pump at a flow rate of 6 to 20 mℓ/min (equivalent EBCT of 3.5 to 12 min). Influent and effluent samples were periodically collected for BrO$_3^-$ and Br$^-$ analysis. Typical operating conditions employed for RSSCT tests are summarised in Table 3.

In order to measure the bromide (surface reduction of BrO$_3^-$ to Br-) adsorbed on the activated carbon surface, the carbon was removed from the RSSCT column after the RSSCT breakthrough experiments, and separated from the aqueous phase by membrane filtration. The activated carbon was further dehydrated by a freeze-dry system (Model 77570, Labconco, Kansas). Then 50 mg of carbon was packed into a glass column (0.3 cm ID x 2 cm) and the carbon was pyrolysed and analysed for Br- by a total halogen analyser (Model TX-10, Mitsubishi, Japan).
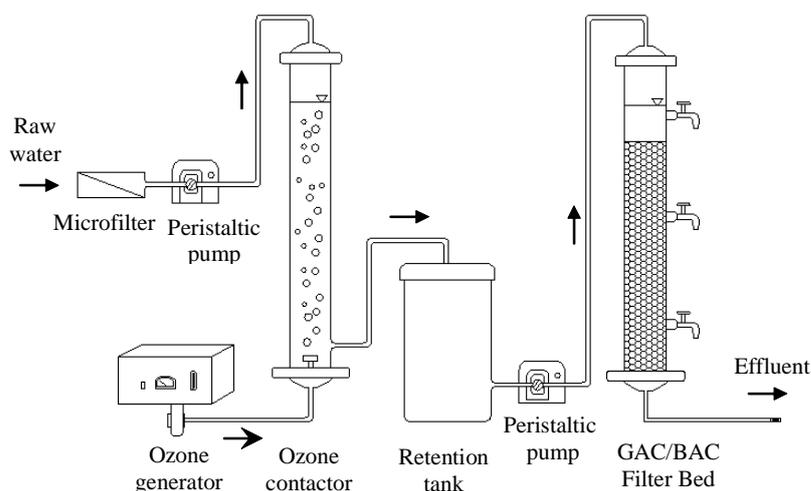
Pilot-scale GAC filter experiments

In the long-term GAC adsorption/reduction experiment, microfiltered and ozonated groundwater with 18 to 163 µg/ℓ of BrO$_3^-$ and 91 to 226 µg acetate-C/ℓ of AOC was continuously passed through the column. The hydraulic loading and EBCT were 10.5 m^3/m^2·h and 15 min, respectively. The operational conditions of the pilot-scale GAC filter are summarised in Table 3.

Analytical method

Water subjected to ozonation was characterised according to DOC, Br$^-$, BrO$_3^-$, and AOC. DOC was measured by the combustion-infrared method using a total organic carbon analyser (Model TOC-5000, Shimadzu, Tokyo, Japan). A Dionex (DX-100) ion chromatograph (IC) measured Br$^-$ and BrO$_3^-$ using an Ionpac column (AS9-HC) and a Dionex guard column (AG9-3C). AOC was measured by a bioassay technique based on a modification of methods described by Van der Kooij and colleagues (Van der Kooij et al., 1989; *Standard Methods*, 1995). The procedure involved sequential growth of two test organisms, namely *Pseudomonas* fluorescence strain P-17 and *Spirillium* strain NOX. The AOC technique has a precision of approximately 15.5 % and a minimum detectable concentration of 5 to 10 µg acetate-C/ℓ.

Results and discussion

Batch results

A kinetic study of BrO$_3^-$ decomposition
Figure 2 displays the batch kinetic removal curves, presented as the amounts adsorbed (q_e) vs. contact time (t), achieved by the five carbons under consideration, for the BrO$_3^-$ single components. It is clear that 8 h are sufficient for attaining the equilibrium for all the adsorption systems. The amounts adsorbed by the five carbons are expressed in two-estimates: Capacity (mg/g or µmole/m^2) and the distribution coefficient, K$_d$ (mℓ/g).

The nearly similar equilibrium time for all the five carbons is not surprising since these carbons should have a high surface area and similar pore size distribution. The kinetics of adsorption of BrO$_3^-$ on the five carbons is described on the basis of Eq. (1):


Figure 1
Schematic diagram of ozone-GAC pilot-plant

TABLE 3 RSSCT and pilot-plant operational conditions		
Parameters	**RSSCT**	**Pilot-plant**
Column pack length (cm)	12.5	120
Column diameter (cm)	1.2	10
GAC particle size (mm)	0.19~ 0.2	0.9~1.2
Mass of GAC (g)	5~6	2450~4900
Pack density (g/cm^3)	0.45~0.6	0.3~0.52
Flow rate (mℓ/min)	6~20	630
EBCT (min)	3.5-12	15

$$q = K_p t^{1/2} \qquad\qquad (1)$$

where:
 q is the instantaneous substrate concentrations on the adsorbent (mg/g)
  K$_p$ is the intraparticle diffusion rate constant
  t is the contact time (h).

The evaluated adsorption rates for intraparticle diffusion, K$_p$, which are useful for comparative purposes, are given in Table 4. The plots covering the initial phase of adsorption (not shown) did not pass through the origin, indicating that pore diffusion may not be the only rate-controlling step in the removal of the adsorbates, especially for the early stages of adsorption. Considering K$_p$, the intraparticle diffusion rate constants listed in Table 4, a similar trend appears for the BrO$_3^-$ relative to the five carbons. On the other hand, the extent of BrO$_3^-$ removal (adsorption capacity) was found to vary significantly from carbon to carbon, ranging from 24 % to almost complete removal with an initial BrO$_3^-$ concentration of 1.5 to 3.5 µmole/ℓ.

Bromate removal capacity
To describe the behaviour of different activated carbons towards BrO$_3^-$ removal, an attempt was made to draw a correlation between the BrO$_3^-$ removal capacity with the inorganic composition and acid-base groups of activated carbons. The inorganic composition
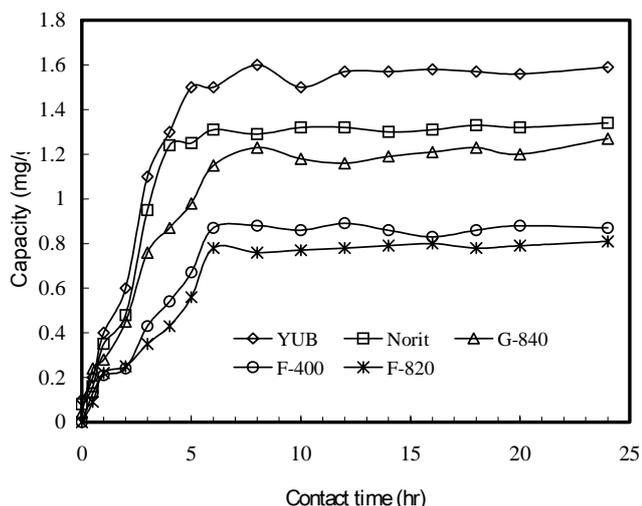
Figure 2
Kinetic plots of BrO_3^- uptake by the five carbons
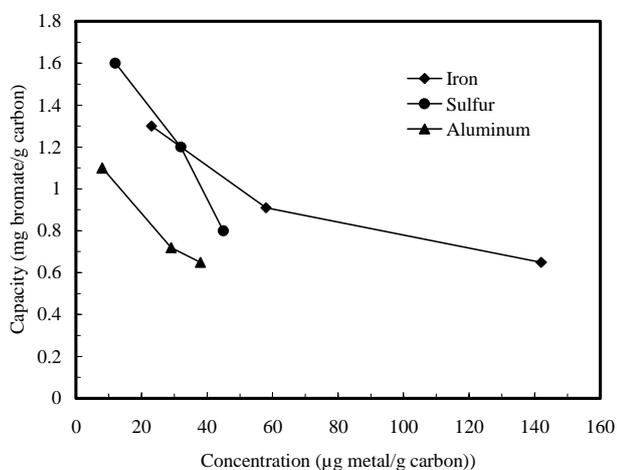
Figure 3
Activated carbon metal concentration and BrO_3^- removal capacities

TABLE 4
Adsorption kinetics parameters for tested carbon samples

Carbon	K_p (mg/g·h^0.5)	q (mg/g)	R^2
YUB	0.462	1.61	0.921
Norit	0.372	1.29	0.952
G-820	0.355	1.23	0.971
F-400	0.254	0.88	0.947
F-820	0.219	0.76	0.956

Conditions: initial BrO_3^- concentration 1.5 to 3.5 μmole/ℓ, and temperature 25ºC

TABLE 5
Acid and basic groups of different carbon samples

Carbon	Acid[d]	Basic[d]	Carboxyl groups[d]
YUB[a]	0.18	0.71	0.07
YUB[b]	0.20	0.62	0.09
Norit[a]	0.21	0.57	0.10
Norit[b]	0.26	0.22	0.13
Norit[c]	0.23	0.14	0.18
G-820[a]	0.28	0.48	0.13
F-400[a]	0.38	0.23	0.16
F-400[b]	0.44	0.18	0.19
F-820[a]	0.39	0.27	0.16

[a] virgin carbon
[b] Nitric acid washed carbon
[c] Thermally regenerated carbon
[d] meq/g carbon

of carbon was found to be an important factor in its ability to inhibit surface reduction of BrO_3^-. An inverse trend was observed between the metal content of these activated carbons and BrO_3^- removal capacities of different activated carbons (Fig. 3). The carbons with the least amounts of these metals, including aluminium, and sulphur, showed the highest BrO_3^- removal capacity suggesting that these inorganic compounds are acting as inhibitors and not catalysts for BrO_3^- removal. This may be attributed to a blockage of active surface groups by these metal oxides or due to oxidation of surface groups by metal groups. Central to the activated carbon surface reduction of BrO_3^- is the role of carbon surface functional groups such as: -SH (sulphides), -S-S (disulphide), and –C=OOH (carbonates).

The chemical characteristics obtained from analysis of the acid-base titration are presented first for virgin carbons and then for acid-washed and thermally regenerated carbon in Table 5. The indicated categories of surface chemical groups are classified according to their acid-base character. A strong correlation was found between these groups and BrO_3^- removal. Activated carbon YUB that was more effective than other activated carbons for BrO_3^- removal was found to possess a much higher number of basic

groups. The least effective carbons, F-820 and F-400, contained the highest number of acid groups and carboxyl groups. These carboxyl groups correspond to the presence of negatively charged carboxylate anionic surface functional groups on the activated carbon. Thus, the ability of carbon to remove BrO_3^- is strongly correlated with the number of basic groups on the surface of the activated carbon.

RSSCT tests

Effect of GAC type on BrO_3^- removal

Figure 4 shows the breakthrough curves of BrO_3^- for five different GACs (F400, F820, Norit, G840, and YUB). The data were obtained from ion-free water spiked with 80 μg/ℓ of BrO_3^-. G840 and F820 carbon had poor BrO_3^- removal capacity, and BrO_3^- breakthrough occurred after 4.5 h (180 bed volumes) and 17 h (620 bed volumes) of operation for G840 and F820 carbon, respectively. After 16 h (700 bed volumes), no BrO_3^- removal was observed on G840. F400 and Norit carbon showed a BrO_3^- breakthrough after about 45 h (1 700 bed volumes) and 80 h (3 400 bed volumes) of operation, respectively. The highest capacity for BrO_3^- removal was
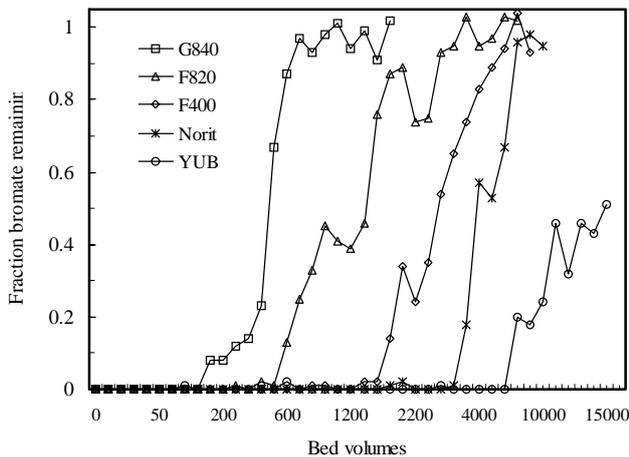
Figure 4
Effect of GAC types on BrO$_3^-$ removal
(Influent BrO3$^-$ = 80 µg/ℓ; EBCT = 5 min)
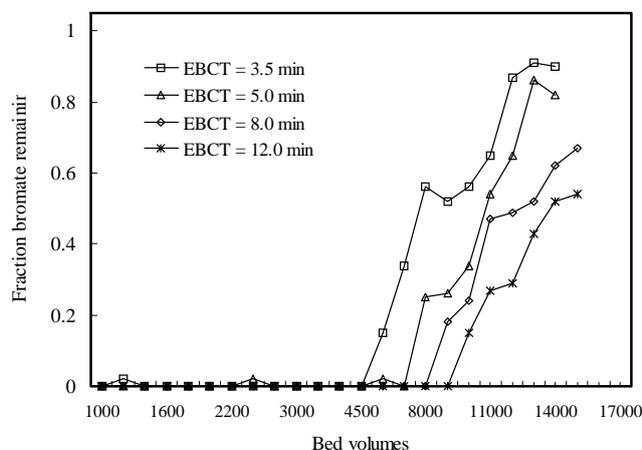
Figure 5
Effect of EBCT on BrO$_3^-$ removal by YUB-GAC
(Influent BrO$_3^-$ = 80 µg/ℓ)
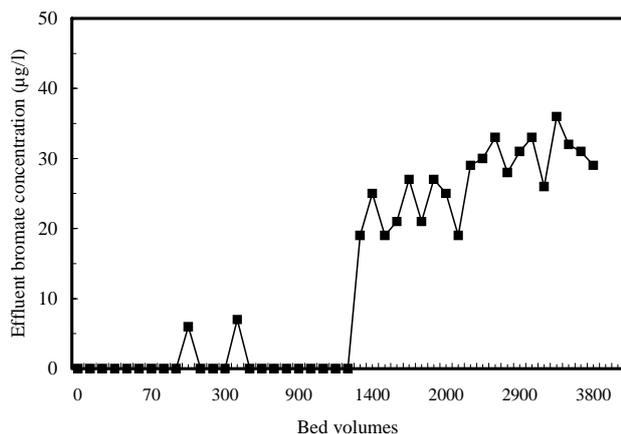
Figure 6
BrO$_3^-$ removal in GAC filters during period (a) influent = 18 to 47 µg/ℓ, (b) influent BrO$_3^-$ = 94 to 163 µg/ℓ

obtained by the YUB carbon with no breakthrough occurring on this carbon until 180 h (7 100 bed volumes) of operation. After 375 h (15 000 bed volumes), approx. 50% of BrO$_3^-$ removal was achieved on this GAC filter.

Siddiqui et al. (1996) found that BrO$_3^-$ removal capacities for different activated carbons are related to the pH values of the iso-electric point (pH$_{pzc}$) and number of acid-base groups on the surface of the activated carbon. Activated carbons with a high number of basic groups and higher pH$_{pzc}$ values showed an increased BrO$_3^-$ removal capacity. Similar trends were observed for GACs tested in this study. The YUB carbon, which was more effective than other GACs for BrO$_3^-$ removal, contained a higher number of basic groups and had a higher pH$_{pzc}$ value, whereas the least effective carbon, F820 carbon, was found to contain the higher number of acid groups and the lowest pH$_{pzc}$ values (Table 2).

Effect of EBCT on BrO$_3^-$ removal

The effect of different EBCTs on BrO$_3^-$ removal was evaluated by varying the water flow rate from 6 to 20 mℓ/min (equivalent EBCT of 3.5 to 12 min). Figure 5 shows the BrO$_3^-$ breakthrough curves for YUB carbon at different EBCTs. From Fig. 7, it is evident that the increase in EBCT produces a more effective reduction of BrO$_3^-$. At 3.5, 5.0, 8.0, and 12.0 min of EBCT, breakthrough of BrO$_3^-$ occurred after 4 700, 7 500, 8 800, and 9 500 bed volumes of influent, respectively. The result indicated that higher BrO$_3^-$ removal capacity is expected at lower EBCT. In other words, high EBCT provides a greater opportunity for BrO$_3^-$ to be adsorbed and reduced to Br$^-$ on the GAC surface. In this study greater than 90% BrO$_3^-$ removal was obtained with an EBCT of 5 to 12 min.

Pilot-plant study

The pilot-plant started operating on 20 November, 2001. BrO$_3^-$ and AOC concentration in the influent of GAC filters was controlled by ozone dosage, Br$^-$ concentration, and DOC content in the influent of the ozonation system. During the study period, BrO$_3^-$ and AOC concentrations in ozonated water fed to the GAC filters ranged from 18 to 163 µg/ℓ and 91 to 226 µg acetate-C/ℓ, respectively. During the first month of operation (from 20 November 2001 to 16 December 2001; filtration of about 1 800 bed volumes), due to low BrO$_3^-$ concentration (18 to 47 µg/ℓ) in the influent, no BrO$_3^-$ was detected (< 5 µg/ℓ) in all but one or two of the effluents. From 17 December 2001 to 17 February 2002, increased BrO$_3^-$ concentrations (94 to163 µg/ℓ) resulted in the BrO$_3^-$ level in the effluent increasing substantially to between 17 and 36 µg/ℓ (Fig. 6). During this period, the treated effluent was unable to meet the WHO recommended safe value criterion of 25 µg/ BrO$_3^-$ (WHO, 1993). The reason for the relatively high BrO$_3^-$ even after GAC treatment in this study was due to the relatively high BrO$_3^-$ concentration in the ozonated effluent. Figure 7 shows a linear relationship between the BrO$_3^-$ influent concentrations and the effluent BrO$_3^-$ content. Asami (1993) reported that removal of BrO$_3^-$ by activated carbon occurs by adsorption, reduction to hypobromite and finally reduction to bromide on the GAC surface. The mechanism of BrO3$^-$ removal by activated carbon was also analysed by Siddiqui et al. (1996), especially in terms of surface conditions and properties of several activated carbons such as powdered activated carbon (PAC) and GAC. They postulated that bromate reduction by activated carbon occurs according to the following reactions:

$$\equiv C + BrO_3^- \rightarrow BrO^- + \equiv CO_2 \qquad (2)$$

$$\equiv C + 2BrO^- \rightarrow 2Br^- + \equiv CO_2 \qquad (3)$$
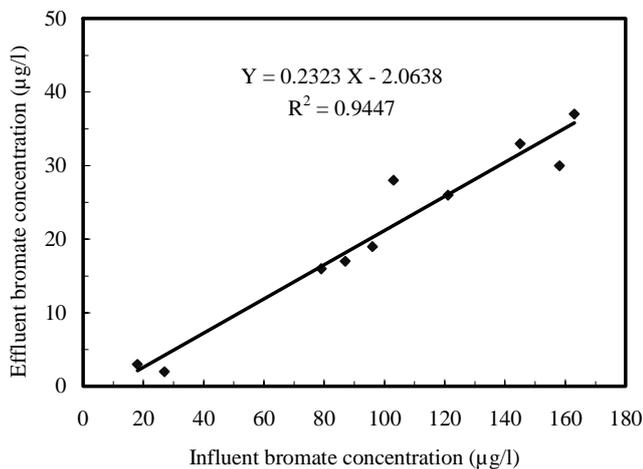
Figure 7
Correlation between the BrO_3^- amount removed by GAC and the influent BrO_3^- concentrations in pilot-plant study
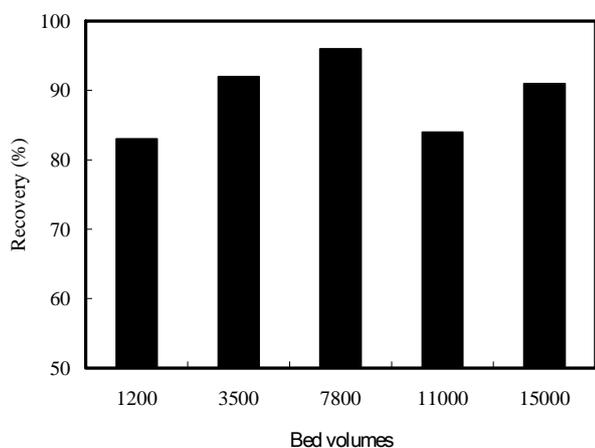
Figure 8
The recovery of bromide species in the GAC column system
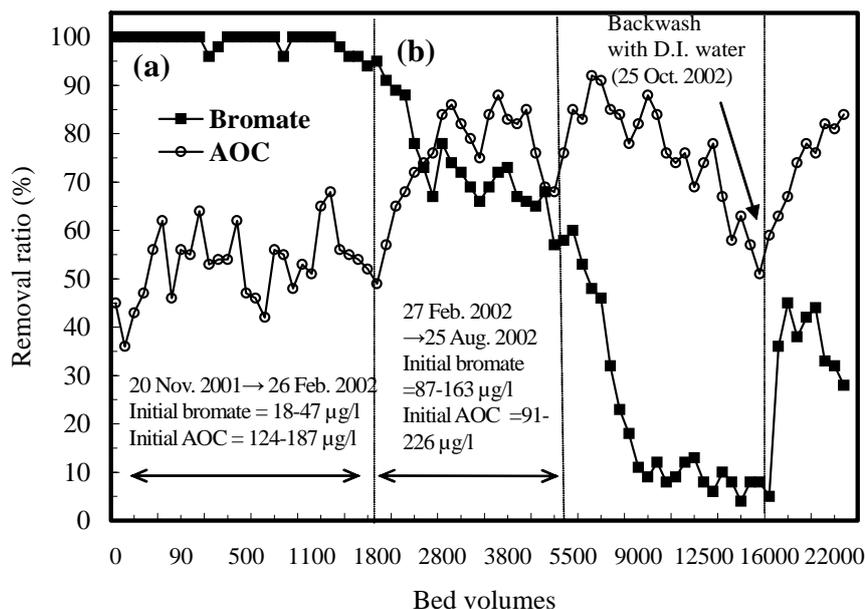
where:
  C represents the activated carbon surface
  CO_2 represents a surface oxide.

During the first 6 months of operation, spent activated carbon was removed from the GAC column, and analysed for Br⁻ species by a total halogen analyser. Measuring the mass of bromide species in the column influent and effluent (including the amount adsorbed on the carbon surface) (Fig. 8), 83 to 96% of the BrO_3^- reduced to Br⁻ was accounted for, confirming the removal mechanism proposed by other researchers (Asami et al., 1999; Yamada, 1993), namely that the chemical reduction of BrO_3^- to Br⁻ is responsible for the BrO_3^- removal by GAC.

According to their results, bromate removal was favoured by a high pH_{zpc}, and a high concentration of surface functional groups. As BrO_3^- is a strong oxidising agent, it can be reasonably reduced by reaction with surface functional groups on activated carbon. Our result that a GAC filter has a low bromate removal capacity after 3 months is attributed to the lack of reactive or reductive functional groups on its surface, that is, functional groups are consumed or oxidised by contact with oxidising constituents during treatment. In contrast, the AOC level was low following GAC treatment. Ozonation prior to GAC resulted in removal efficiencies of over 70%. In the experimental pilot-plant, new GAC was gradually transformed into BAC over a period of 3 to 12 months, which was determined from the bacterial count on the surface of the activated carbon. The bacterial concentration was 5.2 x 10⁸ cfu/g-carbon after 3 months and 2.3 x 10⁹ cfu/g-carbon after 12 months. Monthly changes in the AOC and BrO_3^- removal were observed in the pilot plant during the transition from new GAC into BAC (see Fig. 9). AOC removal ratio was 40 to 65% at the beginning of the experiment and gradually increased after 3 months. However, the BrO_3^- removal ratio started to decrease after 3 months and after 9 months almost no removal occurred. From these results, the breakthrough of BrO_3^- was completed before the breakthrough of AOC in GAC/BAC. These results show that GAC adsorption and biodegradation were effective for AOC control. It should be pointed out that lower BrO_3^- reduction by BAC, possibly due to the organics or biomass adsorbed on GAC, hindered BrO_3^- reduction by GAC either by blocking pores or by adsorption on the activated sites for BrO_3^- reduction.


Figure 9
AOC and BrO_3^- removal in GAC filter during period (a) influent AOC =124 to 187 µg acetate-C/ℓ, influent BrO_3^- = 18 to 47 µg/ℓ, (b) influent AOC = 91 to 226 µg acetate-C/ℓ, influent BrO_3^- = 87 to 163 µg/ℓ

Available on website **http://www.wrc.org.za**

Conclusion

The batch experiments clarified the efficiency of activated carbon adsorption/reduction; BrO_3^- removal depends on the carbon characteristics. The ability of carbon to remove BrO_3^- is strongly correlated with the number of basic groups and the inorganic compounds on the surface of the activated carbon.

Bromate removal using RSSCT columns was significantly faster than in batch tests presumably due to higher diffusion capability. Data from the RSSCT test show that the efficiency of GAC filtration for removing BrO_3^- depends on the type of GAC and empty-bed contact time. The RSSCT testing demonstrated the superior performance of the YUN and Norit carbons over the others. Under RSSCT conditions, GAC provided effective removal over approximately 5 000 bed volumes (YUB carbon). However, the RSSCT testing program was not long enough to ascertain the effects of biological activity (biofilm activity) on BrO_3^- removal. The key concern here is the extent to which a biofilm may interfere with the adsorption step of the overall adsorption/reduction sequence.

In the long-term use of GAC filtration following ozonation, the BrO_3^- removal rate apparently decreased with increasing operating time. These preliminary results indicate that an average of 50 to 80% BrO_3^- can be continuously removed for at least 3 months in a continuous GAC pilot column. However, the BrO_3^- removal ratio started to decrease after 3 months and after 9 months there was almost no removal. This is considered to be due to the lack of reactive or reductive functional groups as a result of oxidation by contact with oxidising constituents during treatment. According to the diffusion mechanism, it is also possibly due to the DOC or AOC being adsorbed on the GAC which hindered BrO_3^- reduction by GAC, either by blocking pores or by adsorbing on the activated sites for BrO_3^- reduction.

The results presented here show that the removal capacity of GAC filtration processes for AOC is high. The GAC system had been in operation for 14 months and it was believed that there was some biological activity inside the GAC bed. It can be predicted that AOC removal is correlated with an increased biomass in the GAC for the future.

Acknowledgements

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