

Removal of bromate and assimilable organic carbon from drinking water using granular activated carbon

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Abstract This study investigated the feasibility of using granular activated carbon (GAC) to remove bromate ion (BrO_3^-) and assimilable organic carbon (AOC) from drinking water through a rapid small-scale column test (RSSCT) method and a pilot-scale study. Results from RSSCT indicated that the GAC capacity for BrO_3^- removal was dependent on the GAC type, empty bed contact time (EBCT), and source water quality. The GAC with a high number of basic groups and higher pH_{pzc} values showed an increased BrO_3^- removal capacity. BrO_3^- removal was improved by increasing EBCT. The high EBCT provides a greater opportunity for BrO_3^- to be adsorbed and reduced to Br^- on the GAC surface. On the other hand, the presence of dissolved organic carbon (DOC) and anions, such as chloride, bromide, and sulfate, resulted in poor BrO_3^- reduction. In the GAC pilot plant, a GAC column preloaded for 12 months achieved a BrO_3^- and AOC removal range from 79–96% and 41–75%, respectively. The BrO_3^- amount removed was found to be proportional to the influent BrO_3^- concentration. However, the BrO_3^- removal rate apparently decreased with increasing operation time. In contrast, the AOC apparently increased during the long-term operation period. This may be a result of the contribution due to new GAC being gradually transformed into biological activated carbon (BAC), and the bacterial biomass adsorbed on GAC surface hindering BrO_3^- reduction by GAC either by blocking pores or adsorbing at the activated sites for BrO_3^- reduction.

Keywords Assimilable organic carbon; bromate; granular activated carbon; ozonation by-products

Introduction

Bromate is a genotoxic carcinogen which may be present in drinking water when ozonation is applied in the treatment of bromide-containing water. According to the literature (Kurokawa *et al.*, 1986), bromate ion has a statistically significant incidence on renal cell tumors in rate F 344. These data led, first of all, to the World Health Organization (WHO, 1993) to classify bromate in class II-B as a carcinogenic potential for humans, then to US and European regulations to include bromate as a new parameter for drinking water. So, the European and the US regulations specify a bromate standard of 10 $\mu\text{g/L}$.

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 ozone dose (Servais *et al.*, 1989).

To eliminate ozonation by-products, GAC is applied as a post-treatment following ozonation. The GAC process results in the adsorption of organic matters, chemical reduction, and mechanical filtration. GAC in actual water treatment processes naturally breeds a bacterial population on its surface, and eventually it works 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 (i.e. BDOC or AOC) are considered to maintain a longer service time before GAC regeneration. The combination of ozonation

and biological treatment with BAC enhances the degradation of organic substances, though it slightly degrades trihalomethane precursors and aldehydes (Cipparone *et al.*, 1997). On the other hand, there have been some reports of BrO_3^- reduction by GAC (Marhaba and Medlar, 1993; Kirisits *et al.*, 2000) and 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 at real plants (Legube, 1996).

At present, the number of reports on activated carbon adsorption and removal of ozonation by-products, especially on BrO_3^- , is 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 behavior of BrO_3^- and AOC in GAC filter. The effect of water sources, carbon type, EBCT and influent concentration on BrO_3^- and AOC removal by activated carbon has been assessed.

Methods

Water sources

Raw groundwaters were collected from the Middle-Western region of Taiwan, which is affected by saltwater intrusion. Historically, specific conductivity in this source water has been as high as 1,600 $\mu\text{s}/\text{cm}$. Dissolved organic carbon (DOC) was under 4 mg/L, and was not particularly high, while its organic content was found to be occupied to a major part by the hydrophobic organics (including humic acid and fulvic acid). The other characteristics of the water sources studied during this research are summarized in Table 1.

Granular activated carbon

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 are summarized in Table 2. The GACs for the batch and RSSCT experiments were prepared by the following procedures. Commercial GACs were pulverized and sieved to obtain 60 x 80 mesh particle sizes, resulting in an average particle diameter of 0.212 mm.

RSSCT experiments

RSSCT experiments were performed using 1.2 cm I.D. glass columns packed with 5–6 g of 60 x 80 mesh size of prepared GACs. The length of the GAC beds was 12.5 cm. Each side of the GAC beds was packed with 2 cm glass beads with comparable particle size to eliminate entrance and exit flow disturbances. Water samples with 100 $\mu\text{g}/\text{L}$ of BrO_3^- were pumped down carefully from a 120-litre plastic tank using a peristaltic pump at a flow rate of

Table 1 Characteristics of water sources

Parameters	CCLW	LGW	WCW
pH	7.4	7.2	7.5
Alkalinity (mg/L as CaCO_3)	134	175	162
Turbidity (NTU)	<1	<1	<1
Conductivity ($\mu\text{s}/\text{cm}$)	687	581	1,480
Sulfate (mg/L)	16.3	13.1	38.3
Chloride (mg/L)	28.7	23.3	63.5
Bromide (mg/L)	1.2	0.7	3.4
Ammonia-nitrogen (mg/L)	<0.02	<0.02	<0.02
Dissolved organic carbon (mg/L)	3.6	3.2	1.2
AOC (μg acetate-C/L)	73	88	36
AOC _{P17} (μg acetate-C/L)	53	74	36
AOC _{NOX} (μg acetate-C/L)	20	14	ND

Table 2 Manufacture specifications of GACs used

Specifications	F-400	F-820	G-840	Norit	YUB
Material	Bituminous coal	Bituminous coal	Coconut shell	Coconut shell	Torbanite
Mean particle size (mm)	1.2	1.2	1.3	1.4	1.2
Total surface area (m ² /g)	950	850	>1,000	950	>1,050
Iodine number (mg/g)	1,000	900	>1,050	1,020	>1,000
Bulk density (g/mL)	0.36–0.38	0.45–0.46	0.31–0.34	0.49–0.52	0.44–0.48
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 Siddiqui *et al.* (1996)

^b pH of isoelectric points (pH_{pzc}) was determined by surface titration method

6–20 ml/min (equivalent EBCT of 3.5–12 min). Influent and effluent samples were periodically collected for BrO₃⁻ and Br⁻ analysis.

Pilot-scale GAC filter experiments

In the long-term GAC adsorption/reduction experiment, microfiltered and ozonated groundwater with 18–163 µg/L of BrO₃⁻ and 91–226 µg acetate-C/L of AOC was continuously passed through the GAC (YUB carbon) column. The hydraulic loading and EBCT were 10.5 m³/m².h and 15 min, respectively.

Analytical method

Water subjected to ozonation was characterized according to DOC, Br⁻, BrO₃⁻, and AOC. DOC was measured by the combustion-infrared method using a total organic carbon analyzer (Model TOC-5000, Shimadzu, Tokyo, Japan). A Dionex (DX-100) ion chromatograph (IC) measured Br⁻ and BrO₃⁻ using an Ionpac column (AS9-HC) and Dionex guard column (AG9-HC). AOC was measured by a bioassay technique based on a modification of methods described by van de Kooij and colleagues (Van der Kooij *et al.*, 1989). The procedure involved sequential growth of two test organisms – *Pseudomonas fluorescens* strain P-17 and *Spirillum* strain NOX. The AOC technique has a precision of approximately ± 15.5% and a minimum detectable concentration of 5–10 µg acetate-C/L.

Results and discussion

RSSCT tests

Effect of GAC type. Figure 1 shows the breakthrough curves of BrO₃⁻ for five different GACs (F400, F820, Norit, G840, and YUB). The data were obtained from ion-free water spiked with 100 µg/L of BrO₃⁻. G840 and F820 carbon had poor BrO₃⁻ removal capacity, BrO₃⁻ breakthrough occurred after 4.5 h (180 bed volumes) and 17 h (620 bed volumes) of operation for G840 and F820 carbon, respectively, and after 16 h (700 bed volumes), no BrO₃⁻ removal was observed on G840. F400 and Norit carbon showed a BrO₃⁻ breakthrough after about 45 h (1,700 bed volumes) and 80 h (3,400 bed volumes) of operation, respectively. The highest capacity for BrO₃⁻ removal was obtained by the YUB carbon, that no breakthrough was obtained on YUB carbon until 180 h (7,100 bed volumes) of operation, and after 375 h (15,000 bed volumes), approximately 50% of BrO₃⁻ removal was also achieved on this GAC filter.

Siddiqui *et al.* (1996) found that BrO₃⁻ removal capacities for different activated carbons are related to their pH values of the isoelectric 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 a higher pH_{pzc} value, whereas the least effective carbon, F820 carbon, was found to contain the highest number of acid groups and the lowest pH_{pzc} values (Table 2).

Effect of DOC. Organic-free deionized water containing DOC (fulvic acid, extracted from the CCLW groundwater) concentrations ranging from 0 to 5.0 mg/L was evaluated for BrO_3^- removal to see if organic matter would compete with BrO_3^- for activated sites on carbon or whether adsorbed natural organic matter would mask potential surface active sites. Figure 2 shows that organic-free water without DOC had the highest BrO_3^- removal when compared with other DOC containing waters. For organic-free water containing no additional DOC, BrO_3^- was not detected in the effluent before 4,000 beds of influent volumes, whereas in the presence of an additional 5 mg/L DOC, BrO_3^- appeared in the effluent within 1,600 volume beds. According to the literature (Siddiqui *et al.*, 1996) BrO_3^- is first adsorbed and then reduced to Br^- , and adsorption of BrO_3^- is critical to BrO_3^- removal.

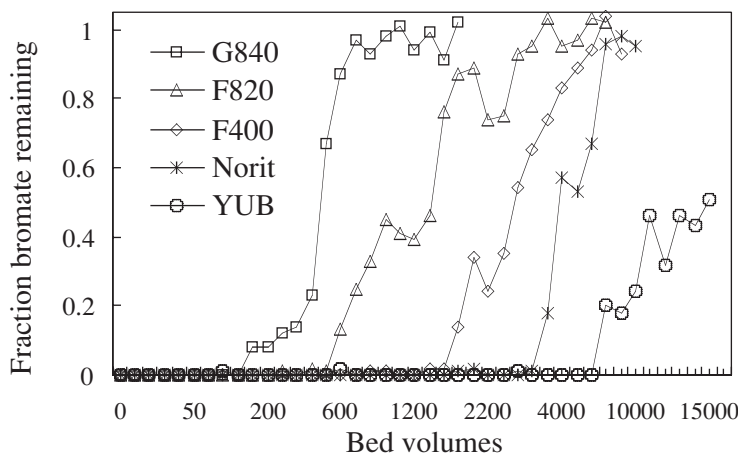


Figure 1 Effect of GAC types on BrO_3^- removal (influent $\text{BrO}_3^- = 100 \mu\text{g/L}$, EBCT = 8 min)

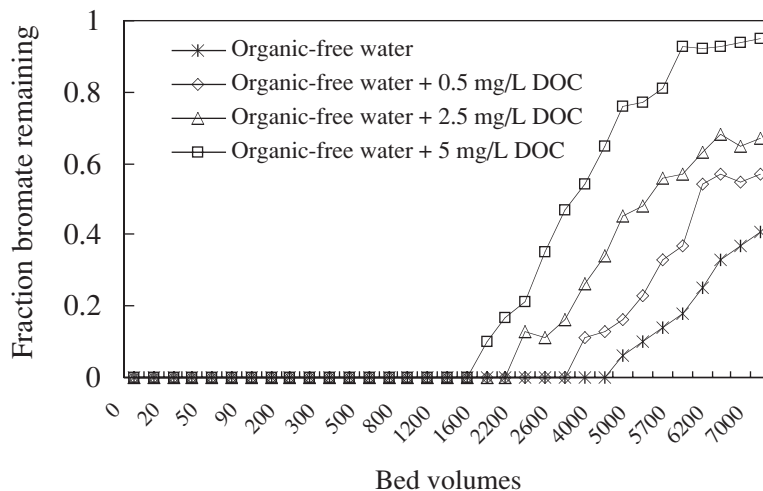


Figure 2 Effect of DOC on BrO_3^- removal. (YUB carbon, influent $\text{BrO}_3^- = 100 \mu\text{g/L}$, EBCT = 8 min)

Thus, the effect of DOC in reducing GAC capacity to remove BrO_3^- may be attributed to DOC competing with BrO_3^- for active sites on the carbon.

Effect of source water. The BrO_3^- breakthrough curves for CCLW, LGW, and WCW waters on YUB carbon are shown in Figure 3. Compared with the result obtained for organic-free deionized water (see Figure 2), the GAC's capacity for BrO_3^- removal was sharply reduced for environmental waters, generally due to competitive adsorption of DOC and anions for the carbon sites as described previously. CCLW (DOC = 3.6 mg/L) showed earlier and steeper initial BrO_3^- breakthrough than LGW (DOC = 1.1 mg/L). This was expected because the pretreatment removed approximately 65% of DOC in LGW resulting in a reduction in competition from DOC and, therefore, a more effective removal of BrO_3^- for LGW. The WCW had low DOC contents (1.2 mg/L) but contained fairly high contents of anions such as chloride, bromide, and sulfate (see Table 1), which may compete with BrO_3^- for adsorption sites of GAC, thus also in this case the BrO_3^- breakthrough occurred earlier. These results, combined with the data in Figure 2, may indicate that water supplies with high levels of DOC or anions can expect poor BrO_3^- removal as a result of competition for the carbon capacity.

Pilot plant study

To clarify the BrO_3^- and AOC behavior in a GAC/BAC filter bed, long-term pilot experiments on BrO_3^- and AOC removal were conducted at the treatment plant. The pilot plant started on November 20, 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 18–163 $\mu\text{g/L}$ and 91–226 $\mu\text{g acetate-C/L}$, respectively. During the first 1 month of operation (from November 20, 2001 to December 16, 2001; filtration of about 1,800 bed volumes), due to low BrO_3^- concentration (18–47 $\mu\text{g/L}$) in the influent (Figure 4), no BrO_3^- was detected ($< 5 \mu\text{g/L}$) in all but one or two of the effluents. From December 17, 2001 to February 17, 2002, increased BrO_3^- concentrations (94–163 $\mu\text{g/L}$) resulted in the BrO_3^- level in the effluent being substantially increased to 17–36 $\mu\text{g/L}$. During this period, the treated effluent was unable to meet the desired criterion of 10 $\mu\text{g/L}$ for WHO recommended safety values. The reason for the relatively high BrO_3^-

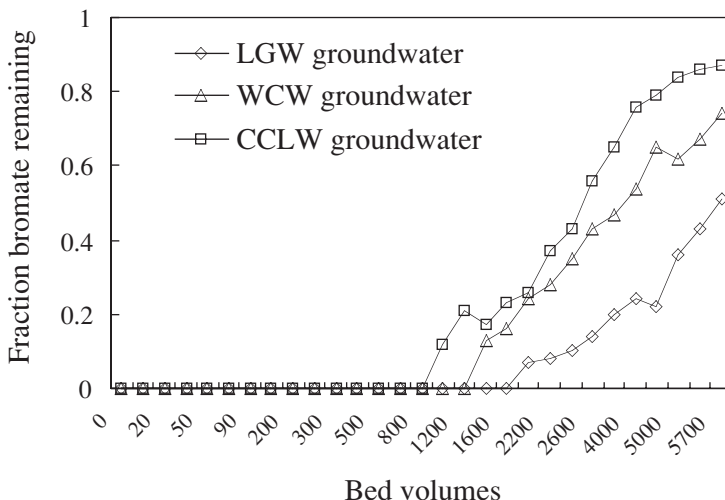
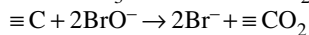
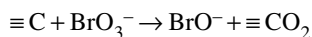


Figure 3 Effect of source water on BrO_3^- removal. (YUB carbon, influent $\text{BrO}_3^- = 100 \mu\text{g/L}$, EBCT = 8 min)

even after GAC treatment in this study would be related to the relatively high BrO_3^- concentration in the ozonated effluent. Asami *et al.* (1999) reported that the removal of bromate ion by activated carbon is adsorbed, reduced to hypobromite and finally reduced to bromide on the GAC surface. They postulated that bromate reduction by activated carbon occurs according to the following reactions:



where $\equiv \text{C}$ represents the activated carbon surface and $\equiv \text{CO}_2$ represents a surface oxide.

During the first 6 months of operation, spent activated carbon was removed from the GAC column, and analyzed for Br species by a total halogen analyzer. Measuring the mass of bromide species in the column influent and effluent (including the amount adsorbed on the carbon surface), 83–96% of the BrO_3^- reduced to Br^- was accounted for supporting the removal mechanism proposed by other researchers (Asami *et al.*, 1999), 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 favored by a high pH_{zpc} , and a high concentration of surface functional groups. As bromate is a strong oxidizing agent, bromate can be reasonably reduced by reaction with surface functional groups on activated carbon. Our result that the GAC filter has a low bromate 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 oxidized by contact with oxidizing constituents during treatment.

In contrast, AOC level was low following GAC treatment. Ozonation through GAC resulted in removal efficiencies of over 70%. In the experimental pilot plant, new GAC was gradually transformed into BAC over a period of 3–12 months, which was determined from the bacterial count on the surface of the activated carbon. Bacterial concentration was 5.2×10^8 cfu/g-carbon at 3 months and 2.3×10^9 cfu/g-carbon after 12 months. Figure 5 shows the micrographs of the GAC surface from new GAC transformed into BAC as seen by scanning electron microscopy (SEM).

Monthly changes in the AOC and BrO_3^- removal were observed at the plant during the transition from new GAC to BAC (Figure 6). AOC removal ratio was 40–65% at the beginning of the experiment and gradually increased after 3 months. However, the BrO_3^-

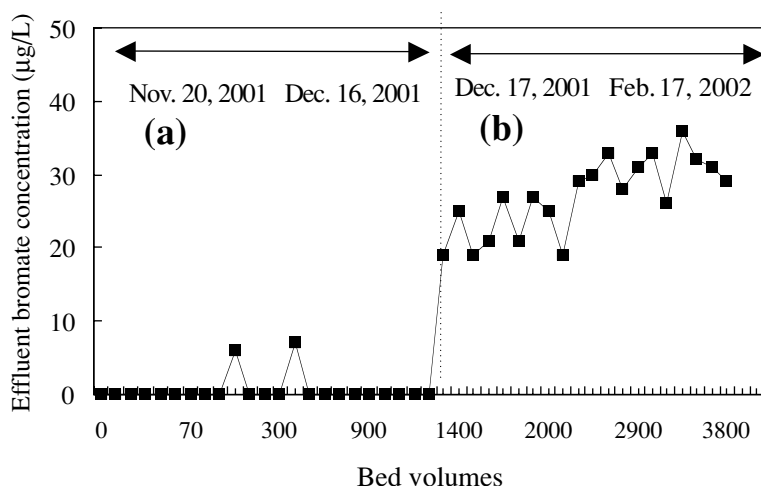


Figure 4 BrO_3^- removal in GAC filters during period (a) influent $\text{BrO}_3^- = 18\text{--}47$ $\mu\text{g/L}$, (b) influent $\text{BrO}_3^- = 94\text{--}163$ $\mu\text{g/L}$

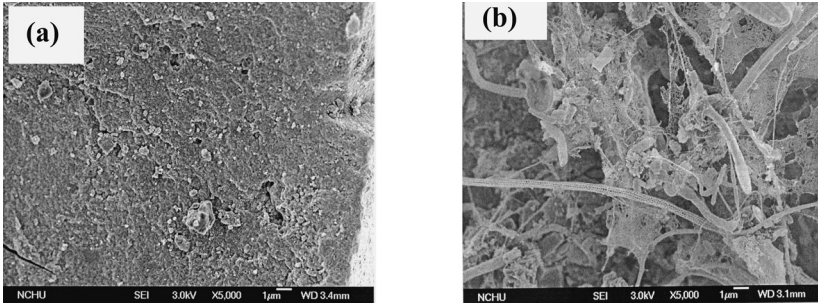


Figure 5 SEM micrograph of GAC surface (a) new GAC, (b) GAC after 9 months

removal ratio started to decrease after 3 months and there was reached almost no removal after 9 months. From these results, the breakthrough of BrO_3^- was completed before the breakthrough of AOC in GAC/BAC. These results showed that GAC adsorption and biodegradation were effective at AOC control. It would be worthwhile pointing 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 adsorbing at the activated sites for BrO_3^- reduction.

Conclusion

Data from RSSCT tests show that the efficiency of GAC filtration for removing BrO_3^- depends on the type of GAC, empty bed contact time, source water, DOC, and inorganic anions. However, a decrease in BrO_3^- removal capacity is not anticipated in an RSSCT column because of breakthrough so that fouling cannot occur thus violating a basic assumption of equal adsorption capacities in RSSCT. Under RSSCT conditions, GAC provided effective BrO_3^- removal over approximately 5,000 bed volumes (YUB carbon). Furthermore, the RSSCT testing program was not long enough to ascertain the effects of biological activity on BrO_3^- removal.

In the long-term use of GAC filtration following ozonation, its bromate removal rate apparently decreased with increasing operation time. These preliminary results indicate that an average of 50–80% BrO_3^- can be continuously removed for at least 3 months in a

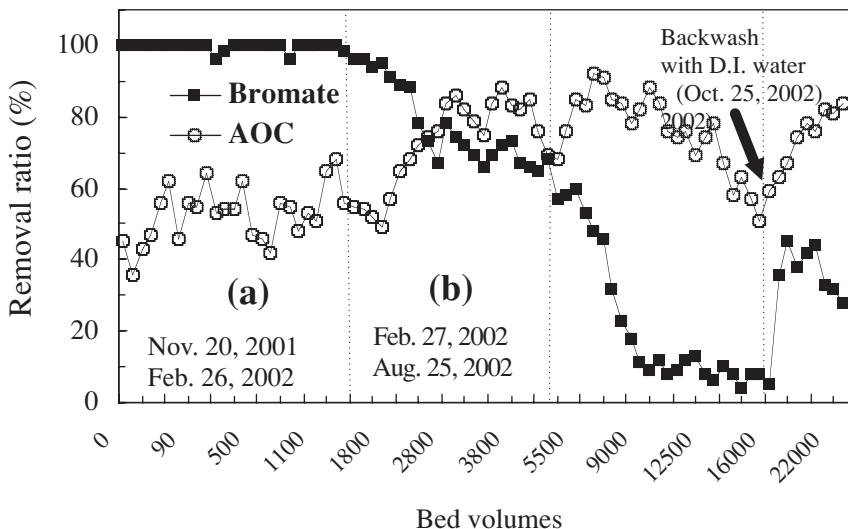


Figure 6 AOC and BrO_3^- removal in GAC filter during period (a) influent AOC = 124–187 μg acetate-C/L, BrO_3^- = 18–47 μg /L, (b) influent AOC = 91–226 μg acetate-C/L, BrO_3^- = 87–163 μg /L

continuous GAC pilot column. However, the BrO_3^- removal ratio started to decrease after 3 months and there was reached almost no removal after 9 months. This is considered to be due to the lack of reactive or reductive functional groups, being consumed or oxidized by contact with oxidizing constituents during treatment. Considering the diffusion mechanism, it is also possibly due to the DOC or AOC adsorbed on GAC hindering BrO_3^- reduction by GAC either by blocking pores or adsorbing at the activated sites for BrO_3^- reduction.

The presented results also 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.

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