Removal of bromide and bromate from drinking water using granular activated carbon

Yong-qing Zhang, Qing-ping Wu, Ju-mei Zhang and Xiu-hua Yang

ABSTRACT

Granular activated carbon (GAC) was used to remove bromide (Br^-) and bromate (BrO_3^-) from drinking water in both bench- and pilot-scale experiments. The present study aims to minimize BrO_3^- formation and eliminate BrO_3^- generated during the ozonation of drinking water, particularly in packaged drinking water. Results show that the Br^- and BrO_3^- levels in GAC-treated water decreased in both bench- and pilot-scale experiments. In the bench-scale experiments, when the empty bed contact time (EBCT) was 5 min, the highest reduction rates of Br^- in the mineral and ultrapure water were found to be 74.9% and 91.2%, respectively, and those of BrO_3^- were 94.4% and 98.8%, respectively. The GAC capacity for Br^- and BrO_3^- removal increased with the increase in EBCT. Reduction efficiency was better in ultrapure water than in mineral water. In the pilot-scale experiments, the minimum reduction rates of Br^- and BrO_3^- were 38.5% and 73.2%, respectively.

Key words | bromate, bromide, granular activated carbon, ozone, reduction

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INTRODUCTION

Ozone, used as an alternative to chlorine in water treatment, has the advantages of significant effectiveness without generation of the disinfection by-products (DBPs) trichloromethane, haloacetic acids and other regulated DBPs. However, a DBP of bromate (BrO_3^-), which is a suspected carcinogen, is generated during the ozonation of bromide (Br^-)-containing water. Thus, a maximum contaminant level of 10 μg/L for BrO_3^- was established by the United States Environmental Protection Agency and by the drinking water standards of China (GB 5749–2006 and GB 8537–2008). A review of BrO_3^- occurrence also indicated that there have been issues of excessive BrO_3^- in drinking water in many countries (Xie & Shang 2006a).

To solve the excessive BrO_3^- problem in drinking water, a number of possible solutions for minimizing BrO_3^- formation, such as adding ammonia (Von Gunten 2003), reducing the pH (Von Gunten 2003), chlorine–ammonia process (Buffle et al. 2004; Wert et al. 2007) and optimizing the ozonation conditions (Bouland et al. 2004; Van der Helm et al. 2005), have been tested. A granular activated carbon (GAC) treatment method also has been used for the removal of BrO_3^- generated during the ozonation of Br^--containing water (Mills et al. 1996; Siddiqui et al. 1996; Bao et al. 1999; Huang et al. 2004a, b; Huang & Cheng 2008). These strategies are always applied for BrO_3^- control in domestic drinking water.

The Chinese standards of drinking natural mineral water (GB 8537–2008) and hygienic specifications of factory for drinking natural mineral water (GB 16330–1996) stipulated that ozone is the only disinfectant except ultra-violet irradiation to be used in the drinking natural mineral water treatment process. A survey showed that 64% of the 108 source water samples of natural mineral water contained Br^- levels above 50 μg/L (Meng 2007). Von Gunten (2003) proposed that in waters with Br^- levels above 50 μg/L, BrO_3^- formation may exceed the maximum contaminant level of the drinking water standard under certain treatment conditions. Thus, the high Br^- concentration in the source water and the ozone application made BrO_3^- a serious issue in the mineral water industry in China.

The present study was performed to elucidate the capacity of GAC to remove Br^- and BrO_3^- from waters in bench-scale experiments. The effects of empty bed contact time (EBCT) and source waters on the levels and reduction rates of Br^- and BrO_3^- were evaluated. The efficiency of GAC in removing Br^- and BrO_3^- from water was also observed in the pilot-scale experiments. The results should provide some new references for controlling the occurrence of BrO_3^- during the ozonation of water with Br^-.

METHODS

Source water

The mineral water used in the study was five gallons of packaged drinking water, containing 7.07 μg/L of Br^- and 6.76 μg/L of BrO_3^-, and was purchased from the market (Guangzhou, China). The ultrapure water, which had no detectable Br^- and BrO_3^-, was produced using deionization and nanopure purification coupled with a Milli-Q purification system (Milli-Q system, Millipore) and had a resistivity of 18.2 MΩ cm. Domestic drinking water, containing 18–20 μg/L Br^- and no detectable BrO_3^-, was used in the pilot-scale experiments.

Bench-scale experiments

The bench-scale experiments were performed using a 4.5 cm × 80 cm glass column packed with 400 g GAC. The GAC used in the experiment was the same as the GAC3 reported by Zhang *et al.* (2011) with 648.42 mg/g iodine adsorption value. The length of the GAC bed was 38 cm. Both the mineral and ultrapure waters were used as source waters. The source waters were spiked with various levels of Br^- or BrO_3^- to produce test solutions, which were carefully pumped into and out of the GAC column using YZ1515x peristaltic pumps (Baoding Longer Precision Pump Co., Ltd, Hebei, China). The EBCT was controlled by the water flow rate using the peristaltic pumps. The influent and effluent samples were periodically collected for Br^- and BrO_3^- detection and were taken in parallel every time.

Pilot-scale experiments

The pilot-scale experiments were carried out using domestic drinking water as the source water and were performed in a set of 2 T/h equipment for mineral water treatment. The equipment was as follows: three storage tanks for the source water, three sets of ultra-violet irradiation apparatus, a tank of sand for filtration, two tanks of GAC, a set of instruments for fine filtration comprising sequential 10, 5, 1 and 0.22 μm filters, a set of ozone generation instruments, two sets of ozone contact instruments, apparatus for the addition of CO_2 and a storage tank for the treated water.

The pilot-scale experiments for determining GAC capacity for Br^- reduction were initiated after the addition of various concentrations of KBr^- into the source water until the mixture was fully stirred, then the solutions were treated by using the sand filter, GAC, fine filter and ozonation. The samples were periodically collected and examined before and after GAC treatment. Two samples were taken in parallel every time. The GAC used in the experiment was the same as the GAC11 reported by Zhang *et al.* (2011) with 953.27 mg/g iodine adsorption value.

The pilot-scale experiments for detecting GAC capacity for BrO_3^- reduction was initiated after the addition of 60 μg/L of $KBrO_3^-$ into the water source until the mixture was fully stirred, then the solution was treated as in the Br^- reduction experiments. The BrO_3^- concentration in the influent sample of the GAC system was controlled using the ozone dose during ozonation. The samples were periodically collected and examined before and after GAC treatment. Two samples were taken in parallel every time. The GAC used in the experiment was the same as the GAC2 reported by Zhang *et al.* (2011) with 832.96 mg/g iodine adsorption value.

Analytical method

Br^- and BrO_3^- levels were measured using a Dionex ion chromatograph (ICS1500) equipped with AS19 analytical/ AG19 guard columns, an ASRS300 anion suppressor and an AS40 automatic sampler. A value of 0.50 μg/L was used to facilitate statistical analysis if the detected result was lower than the detection limit of 1 μg/L. The reduction

rates of Br^- or BrO_3^- were calculated as: ([influent Br^- or BrO_3^-] – [effluent Br^- or BrO_3^-])/([influent Br^- or BrO_3^-]) × 100%.

RESULTS AND DISCUSSION

Bench-scale experiments

Removal of Br^- from the mineral water

In mineral water with an initial Br^- content of 50.00 and 105.59 μg/L, the Br^- contents of the treated water were respectively 36.84 and 66.14 μg/L after 2 min, and 24.09 and 43.14 μg/L after 5 min. When the initial Br^- was 192.57, 264.47 and 596.13 μg g/L, the Br^- contents of the treated water were 59.56, 114.59 and 149.39 μg/L after 5 min. The Br^- reduction rates were between 26.3 and 41.9% after 2 min and between 51.8 and 74.9% after 5 min (Figure 1).

Other studies suggested that when the Br^- levels in water are greater than 50 μg/L, the BrO_3^- produced under certain treatment conditions may exceed the drinking water standard of 10 μg/L (Amy *et al.* 2000; Von Gunten & Pinkernell 2000). Thus, this method cannot remove the excessive BrO_3^- when the initial level of Br^- in the source water is greater than 190 μg/L. Other methods should be

considered to control BrO_3^- produced during the ozonation of drinking water with Br^-.

Removal of Br^- from the ultrapure water

In ultrapure water with an initial Br^- content of 30.62 and 91.27 μg/L, the contents of the treated water were respectively 11.71 and 24.28 μg/L after 2 min, and 11.56 and 16.35 μg/L after 5 min. When the initial Br^- was 192.60, 395.98 and 599.39 μg/L, the Br^- contents of the treated water was respectively 18.23, 34.95 and 72.19 μg/L after 5 min. The Br^- reduction rates were between 61.74 and 86.58% after 2 min and between 62.26 and 91.17% after 5 min (Figure 2).

The GAC capacity for Br^- reduction was better in the ultrapure water than in the mineral water, which may be attributable to the more complex properties of the latter compared with the former. Meanwhile, GAC efficiency for Br^- removal increased when EBCT was increased for both mineral and ultrapure waters. This may provide greater chances for GAC to absorb Br^-.

Removal of BrO_3^- from the mineral water

In the mineral water with an initial BrO_3^- content of 18.12, 31.48, 57.40, 81.10 and 110.01 μg/L, the BrO_3^- levels in the treated water were respectively 4.36, 7.81, 14.29, 20.39 and 10.47 μg/L after 2 min, and 0.71, 3.33, 3.51, 12.69 and
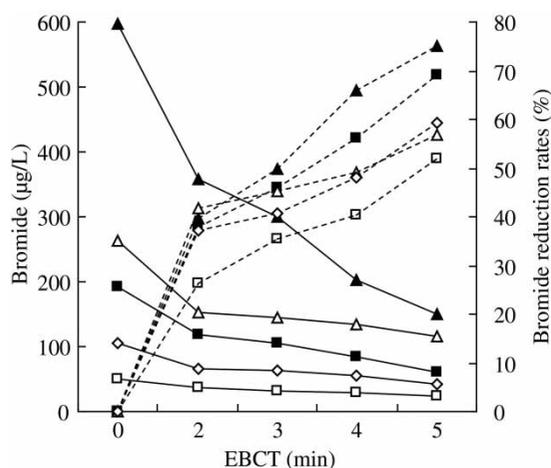
Figure 1 | Effect of GAC on Br^- in mineral water. Unbroken lines: Br^- (μg/L); dotted lines: Br^- reduction rates (%). Initial Br^- in water: (□) 50.00 μg/L; (◇) 105.59 μg/L; (■) 192.57 μg/L; (△) 264.47 μg/L; and (▲) 596.13 μg/L.
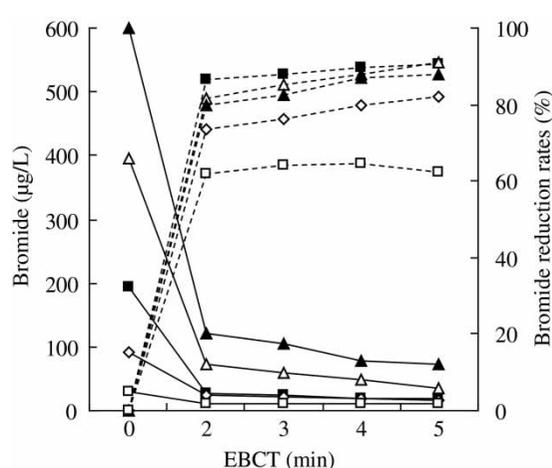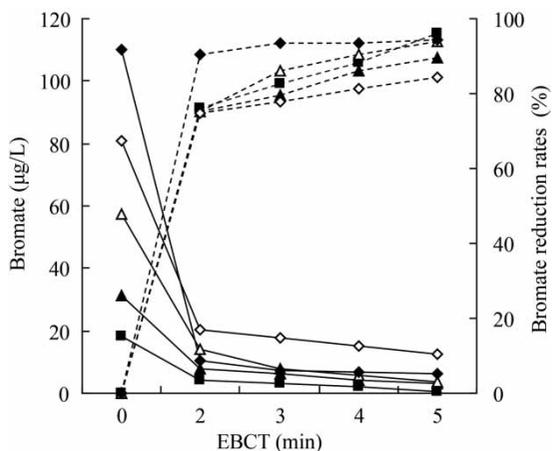

Figure 2 | Effect of GAC on Br^- in ultrapure water. Unbroken lines: Br^- (μg/L); dotted lines: Br^- reduction rates (%). Initial Br^- in water: (□) 30.62 μg/L; (◇) 91.27 μg/L; (■) 192.60 μg/L; (△) 395.98 μg/L; and (▲) 599.39 μg/L.

6.13 µg/L after 5 min. The removal rates were greater than 75% when EBCT was longer than 2 min, and the maximum reduction rate was 94.4% (Figure 3). With increasing EBCT, the BrO_3^- levels of the treated water decreased, and the removal rates increased. These results were consistent with the report of Huang et al. (2004a, b) stating that BrO_3^- removal improves when EBCT is increased.
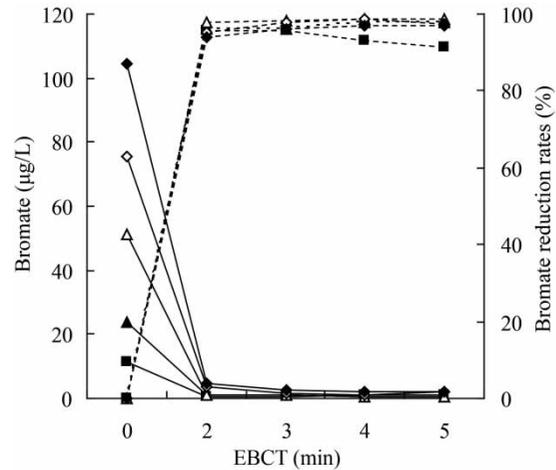
Removal of BrO_3^- from the ultrapure water

In the ultrapure water, the initial BrO_3^- contents were respectively 11.23, 24.05, 51.05, 75.63 and 104.65 µg/L. When EBCT was 2 min, the BrO_3^- levels in the treated water were efficiently removed, and the desired criterion of less than 10 µg/L was achieved. The reduction rates were between 87.8 and 98.8% after 5 min (Figure 4). When EBCT was increased, the BrO_3^- levels of the treated water decreased, and the removal rates increased.

These results suggest that the GAC capacity for BrO_3^- and Br^- removal was better in ultrapure water than in mineral water. This result may be attributed to the competitive adsorption between Br^-/BrO_3^- and natural organic matter or other anions, such as Cl^-, Br^- and SO_4^{2-}. Competitive adsorption has been reported to reduce the capability of GAC for absorbing BrO_3^- (Mills et al. 1996; Bao et al. 1999; Huang et al. 2004a, b; An et al. 2008).

Figure 3 | Effect of GAC on BrO_3^- in mineral waters. Unbroken lines: BrO_3^- (µg/L); dotted lines: BrO_3^- reduction rates (%). Initial BrO_3^- in water: (■) 18.12 µg/L; (▲) 31.48 µg/L; (△) 57.40 µg/L; (◇) 81.10 µg/L; and (◆) 110.01 µg/L.

Figure 4 | Effect of GAC on BrO_3^- in ultrapure water. Unbroken lines: BrO_3^- (µg/L); dotted lines: BrO_3^- reduction rates (%). Initial BrO_3^- in water: (■) 11.23 µg/L; (▲) 24.05 µg/L; (△) 51.05 µg/L; (◇) 75.63 µg/L; and (◆) 104.65 µg/L.

Pilot-scale experiments

Removal of Br^-

Domestic drinking water with different initial BrO_3^- content was used as the source water. The results show that the Br^- concentrations in the treated water decreased (Table 1). Therefore, GAC may be used for the removal of Br^- from source waters.

Removal of BrO_3^-

The source water was used to make a solution containing 60 µg/L of BrO_3^-. Table 2 shows that when the ozone concentration is 0.73 mg/L, the concentration of produced BrO_3^- increased steeply and exceeded 10 µg/L standard. Nevertheless, the excessive amount of BrO_3^- decreased to less than 10 µg/L after GAC treatment. Therefore, GAC may be used to eliminate the BrO_3^- generated during the ozonation of drinking water.

Table 1 | Effects of GAC on Br^- in water

Influent content (µg/L)	Effluent content (µg/L)	Reduction rates (%)
65.87	37.84	42.56
80.51	47.37	41.17
97.10	59.67	38.54

Table 2 | Effect of GAC on BrO_3^- in water

Ozone doses (mg/L)	Influent content (µg/L)	Effluent content (µg/L)	Reduction rates (%)
0.11	0.50	0.50	0.00
0.30	2.77	0.50	81.95
0.43	6.27	1.43	77.25
0.55	5.84	1.57	73.15
0.73	18.80	1.41	92.48

For both Br^- and BrO_3^- the reduction rates were lower in the pilot-scale than in the bench-scale experiments. The variations in the results may be attributable to the different source waters and GAC used in the experiments.

In the present study, GAC appeared to be capable of reducing both Br^- and BrO_3^- concentrations in drinking water, which may be attributable to the similar inorganic characteristics of Br^- and BrO_3^-. Nevertheless, the removal mechanism of BrO_3^- using GAC should be different from that of Br^-. The process of BrO_3^- removal by GAC was reported to initially be an adsorption, followed by a two-step reduction reaction (Siddiqui *et al.* 1996). A limited amount of data is available on investigations of the GAC mechanism for Br^- elimination. Therefore, studying the GAC mechanisms for Br^- removal is necessary.

Both the physical and chemical effects simultaneously act on the adsorption–reduction process during the GAC treatment for BrO_3^- reduction (Huang & Cheng 2008). Source water quality and EBCT also affect GAC capacity for BrO_3^- removal (Bao *et al.* 1999). Therefore, ascertaining the optimum EBCT and investigating how both GAC and water properties affect the removal of Br^- and BrO_3^- are important.

In addition, other strategies for the reduction of the BrO_3^- generated during the ozonation of the water with Br^-, such as ultra-violet irradiation (Meunier *et al.* 2006), ion exchange membrane bioreactor (Matos *et al.* 2005) and BrO_3^- reduction using zerovalent iron (Fan *et al.* 2006; Xie & Shang 2006b) and TiO_2 (Noguchi *et al.* 2002), are also available. However, a number of problems, such as high cost and the quality of the treated water, limit the use of these methods, especially for packaged drinking water.

Based on the current experiments, GAC was effective in removing Br^- and BrO_3^- contents from drinking water. GAC technology may be used to reduce BrO_3^- formation and to eliminate BrO_3^- generation during the ozonation of water with Br^-. However, further investigations on the actual conditions and influence factors of using GAC technology should be conducted because of the limited data available.

CONCLUSIONS

In the present study, Br^- and BrO_3^- levels in the solutions of water sources were efficiently eliminated using GAC. In the bench-scale experiments, the removal contents and rates of Br^- and BrO_3^- increased with increasing EBCT, and the GAC capacity to reduce Br^- and BrO_3^- contents was better in ultrapure water than in mineral water. Although the effects of GAC on Br^- and BrO_3^- were weaker in the pilot-scale experiments than in the bench-scale experiments, GAC still showed the capability of eliminating Br^- and BrO_3^- contents in the pilot-scale experiments. The minimum reduction rates of Br^- and BrO_3^- were 38.5% and 73.2%, respectively. Therefore, GAC can be employed in water treatment facilities to minimize BrO_3^- formation by decreasing Br^- contents and to eliminate the BrO_3^- generated in ozonated water.

ACKNOWLEDGMENTS

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