



Pilot study on bromate reduction in ozonation of water with low carbonate alkalinities by carbon dioxide

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Abstract

A pilot study was carried out to explore the application of carbon dioxide for pH depression in a bubble column and its ability to inhibit bromate formation for water with a low alkalinity. Results showed that in the absence of ammonia, CO₂ was capable of reducing bromate 38.0%–65.4% with one-unit pH depression. CO₂ caused a slightly lower bromate reduction (4.2%) than did H₂SO₄ when the pH was depressed to 7.4, and a more pronounced lower reduction (8.8%) when the pH was depressed to 6.9. In the presence of 0.20 mg/L-N ammonia, bromate was largely inhibited with 73.9% reduction. When the pH was depressed to 7.4, CO₂ and H₂SO₄ showed an 11.3% and 23.5% bromate reduction respectively, demonstrating that the joint use of CO₂ and ammonia might be a plausible strategy of blocking all three bromate formation pathways. CO₂ could be applied through the aeration diffuser together with ozone gas, resulting in a similar bromate reduction compared with the premixing method through Venturi mixer.

Key words: ozone; bromate; carbon dioxide

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Introduction

Ozonation has become widely used in drinking water treatment due to ozone's strong disinfection capabilities on *Cryptosporidium parvum* oocysts and *Giardia lamblia* oocysts, which have strong resistance to chlorine. However, ozonation of bromide-containing water produces bromate, a human carcinogen regulated in the United States, European Union, and other countries, including China. The maximum level of bromate in drinking water is currently set at 10 µg/L (US EPA, 1998; European Union, 1998; China Ministry of Health, 2006). These regulations promoted intensive research on alternative bromate control measures and corresponding mechanisms.

Bromate control measures were classified into two categories: bromate removal after formation and bromate minimization during formation (Xie and Shang, 2006). Bromate removal can be achieved by using activated carbon (Shi et al., 2009), ferrous ions (Dong et al., 2009), zerovalent iron (Westerhoff, 2003), humic substances (Xie et al., 2008), and electrochemical reduction (Kishimoto and Matsuda, 2009). These measures demonstrate bromate removal capabilities, but are unlikely to be applied in practice due to their high costs, long reaction times, impacts on subsequent processes, and necessity for additional processes for the introduction of chemical reagents (Xie

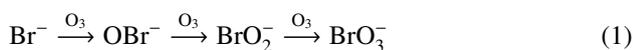
and Shang, 2006). Bromate minimization methods during formation include the optimization of ozone dosage (Guo et al., 2007), and pH depression or ammonia addition (von Gunten, 2003). It was reported that pH depression was capable of reducing bromate by 50%–63% for a one-unit pH decrease (Xie and Shang, 2006), and ammonia addition may achieve a 0–30% reduction of bromate formation (Siddiqui et al., 1994). Mechanisms of bromate minimization by pH depression and ammonia addition were revealed in several publications (von Gunten and Hoigne, 1994; von Gunten, 2003). Based on these literature, a simplified mechanism was drawn as Reactions (1), (2), and (3), showing the three bromide formation pathways. Bromide is initially oxidized either directly by ozone or indirectly by hydroxyl radical. Ozone oxidizes Br⁻ to HOBr/OBr⁻, a decisive intermediate in bromate formation. HOBr and OBr⁻ can be further oxidized by radicals (defined as the direct/indirect pathway), but only OBr⁻ can be oxidized by ozone (defined as the direct pathway). Hydroxyl radicals oxidize Br⁻ to Br₂, which is either oxidized by ozone or converted to OBr⁻ and subsequently oxidized by radical or ozone, collectively defined as indirect pathway. pH depression blocks the direct pathway by favoring the equilibrium of OBr⁻→HOBr and suppressing further oxidation of OBr⁻ by ozone. Ammonia addition blocks the direct and direct/indirect pathways by reacting with HOBr to form bromamines and suppressing further oxidation of OBr⁻

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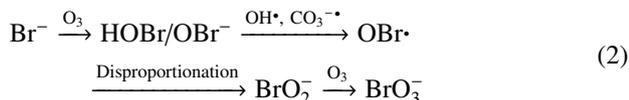
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by ozone and oxidation of HOBr/OBr⁻ by radicals as the following Reactions (1), (2), and (3):

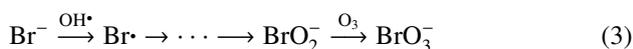
Direct



Direct/Indirect



Indirect



where, the simplified bromate formation pathways was from von Gunten (2003). Dashed line in the indirect pathway indicates a simplification of three possible paths from Br[•] to BrO₂⁻.

pH depression does not introduce external pollutants like ammonia addition does. It is preferable in water with low alkalinities because of its low dosage of acid. However, lowering pH might cause the negative effect of erosion, especially in the case of aged distribution pipelines. Therefore, moderate pH depression with more efficient bromate reduction is desirable. The most common method is the addition of an acid, such as HCl, or an H₂SO₄ solution.

This study recommends an alternative way of adding CO₂ for pH depression. The CO₂ lowers pH value as well as introduces carbonate with a complicated impact on bromate formation. It scavenges hydroxyl radicals quickly (Buxton et al., 1988) and blocks the indirect pathway of bromate formation while producing CO₃^{•-} that promotes the direct/indirect pathway. Kinetic simulations showed that bromate formation through the OH radical mechanism is nearly independent of total carbonate concentrations. These simulations also showed that for a pH of 8.0, no systematic variation would be observed in the bromate formation for different alkalinities. The calculated fraction of OH radicals scavenged by CO₃²⁻ varied between 50% (1 mmol/L CO₃²⁻) and 90% (10 mmol/L CO₃²⁻) (von Gunten and Hoigne, 1994). Hofmann and Andrews (2006) suggested that carbonate alkalinity partially negates the increase of bromate formation at high pHs because of the increased concentration of OH[•], but Song et al. (1996) suggested that carbonate alkalinity probably enhances bromate formation because it helps stabilizing and maintaining ozone concentrations in the solution. These conflicting suggestions require more investigation. Since the oxidation of HOBr/OBr⁻ by carbonate radicals to BrO[•] is not well established and has only been assessed qualitatively so far (von Gunten, 2003), a pilot study was carried out in this research to explore the application of CO₂ as a pH-depression reagent for bromate minimization in water with a low alkalinity.

1 Materials and methods

1.1 Characteristics of source water

The source water was taken from the tap in Shenzhen, China, and was spiked with a KBr solution. The main parameters of the source water were subject to small variations in this research. The characteristics of the source water were pH 8.0–8.3; total organic carbon (TOC) 1.20–2.45 mg/L; temperature 28–31°C; total carbonate alkalinity 15.5–22.1 mg/L as CaCO₃; turbidity 0.2–0.4 NTU; NH₄⁺ < 0.2 mg/L-N; and Br⁻ 216–235 μg/L.

1.2 Pilot scale experiments

The schematic diagram of the experimental apparatus is shown in Fig. 1. The source water was stored in an 8 m³ source water tank, and two submerged pumps were turned on for at least 3 hours before the experiment was carried out to achieve a complete mixing of the spiked KBr solution. The source water was pumped into the ozone contact column (made of polymethyl methacrylate, 164 mm in inner diameter, 4.5 m in height) by a centrifugal pump with the flow rate 2.4 m³/hr. The column effluent pipe was designed to ensure an approximate 4.0 m water depth in the column when no gas was supplied. Pure oxygen was supplied by a cylinder to an ozone generator (Qingdao Guolin, CF-G-3-30G, China), which provided a 0.20 m³/hr gas flow rate with 8%–10% (*m/m*) ozone into the column through a diffuser made by a sintered sand core funnel (G4 type with 3–4 μm pores). The ozone generator was turned on for over 20 minutes to achieve a

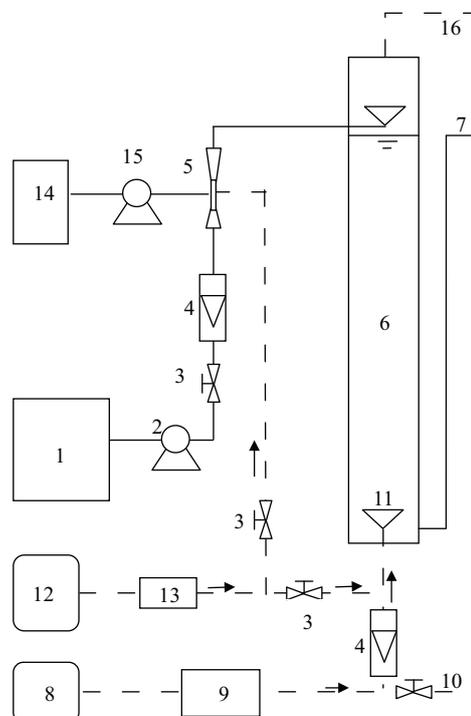


Fig. 1 Experimental setup. (1) source water storage tank (with 2 submerged pumps inside); (2) centrifugal pump; (3) valve; (4) rotary flowmeter; (5) venturi mixer; (6) ozone contact column; (7) effluent; (8) O₂ cylinder; (9) ozone generator; (10) ozone gas sampling point; (11) diffuser; (12) CO₂ cylinder; (13) mass flowmeter; (14) chemicals storage tank; (15) peristaltic pump; (16) off-gas.

stable production of ozone before it was introduced into the column. Influent and effluent ozone gas was sampled to determine the gaseous ozone concentration and ozone dosage. The ozone dosage in this study was about 5.25 mg/L throughout the whole experiment if not specified otherwise.

Pure CO₂ gas was supplied from a cylinder into the diffuser mentioned above if not specified otherwise, or into a Venture mixer when specified. The flow rate was controlled by an auto-adjusting mass flowmeter. An H₂SO₄ solution was pumped into a Venturi mixture by a peristaltic pump (BT100-2J, Baoding Longer Precision Pump, China) when required. Jar tests showed that bromate formation was not affected by SO₄²⁻ during ozonation.

1.3 Analytic methods

Bromide and bromate concentrations were determined by using an ion chromatographer (DIONEX ICS3000 coupled with column anion AS19, USA) with a detection limit of 0.8 µg/L for both bromide and bromate. Carbonate alkalinity and bicarbonate alkalinity was determined by Potentiometric titration. pH and TOC was analyzed by a Mettler Toledo FE20 Desktop pH Meter (USA) and a Jena multi N/C 3100 TOC (Germany), respectively. Ozone concentrations in gas and water were analyzed using iodometry.

2 Results and discussion

2.1 Effluent sampling

To ensure a stabilized effluent concentration of bromate, an 11-minute interval (about 5 times of the hydraulic retention time of the contact column) was adopted before sampling. Figure 2 shows that the bromate and bromide concentrations were subject to only small changes 11 min after ozone was applied either with or without CO₂ addition. Effluent gas was sampled from the 11th to the 21st minute every 2 min. The experiment showed that the standardized deviations of the 6 samples were 4.21 µg/L

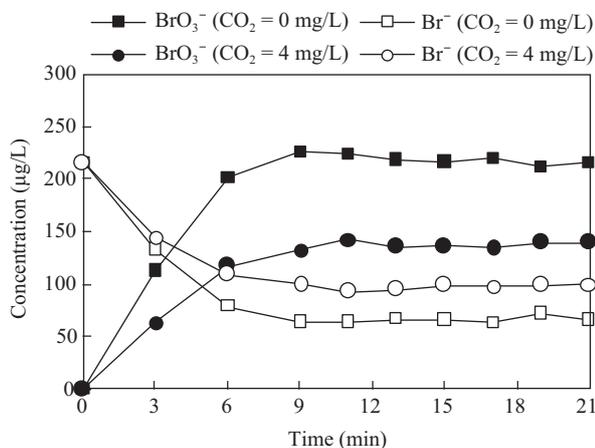


Fig. 2 Variation of effluent bromate and bromide concentration with operation time. Source water: Br⁻ 216 µg/L; NH₄⁺ < 0.02 mg/L-N; pH 8.05; ozone dosage 5.25 mg/L.

for bromate and 3.21 µg/L for bromide, demonstrating a good consistency among the samples.

2.2 Bromate minimization by CO₂ addition

The impact of CO₂ dosages on bromate formation is shown in Fig. 3. With the increase of CO₂ dosage, bromate continued to decrease but less rapidly in the case of higher CO₂ dosages. Bromate was reduced by 34% with a 4 mg/L CO₂ addition and 54% with an 8 mg/L CO₂ addition. When no CO₂ was applied, the pH decreased from 8.05 to 7.75 after ozonation. When CO₂ was applied, the pH shared a similar decreasing pattern to bromate, decreasing rapidly to 6.99 with an 8 mg/L CO₂ addition, followed by a slower decrease rate when a higher CO₂ dosage was applied. Bromide concentration increased with the decrease of bromate. It should also be noted that the total bromine of both bromate and bromide (hereinafter referred to as total inorganic bromine) had an 8.89% decrease from 202.6 to 184.6 µg/L when 4 mg/L CO₂ was added, but no further decrease was found when a higher CO₂ dosage was applied. This might be due to the longer lifetime of HOBr under depressed pH conditions and a trade-off between lower bromate formation and higher total organic bromine (TOBr) formation (Song et al., 1997).

Three additional sets of experiments were carried out every 1 or 2 days under identical conditions except for perhaps slightly differing characteristics of source water and adjusted CO₂ dosages to achieve a moderate pH drop. To facilitate analysis, the inhibitory effect of bromate was expressed as normalized bromate concentration with the bromate in the CO₂ free case set to be 1.0 in each set of experiment. Figure 4 shows the good linear relationships between pH and bromate formation in all sets of experiments. A unit of pH decrease will cause a bromate formation decrease, ranging from 38.0%–65.4%. The result was comparable to the result of Xie and Shang (2006), that concluded that there would be a reduction of 50%–63% for a one-unit pH decrease. A collective

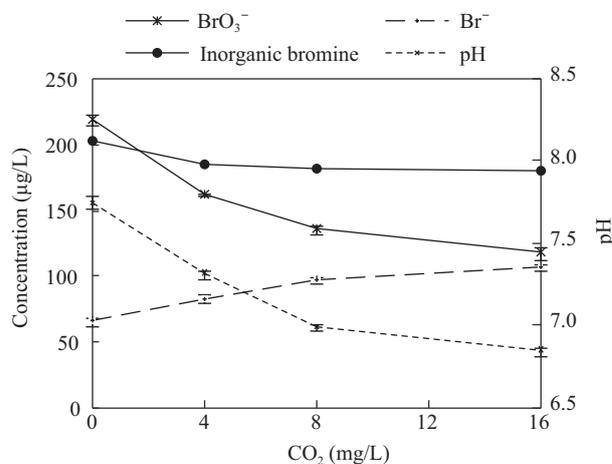


Fig. 3 Impact of CO₂ dosage on pH and bromate formation. Source water: Br⁻ 216 µg/L; NH₄⁺ < 0.02 mg/L-N; pH 8.05; ozone dosage 5.25 mg/L. Data are expressed as the average of six samples, error bars giving the standard deviations. Inorganic bromine included bromide and bromate.

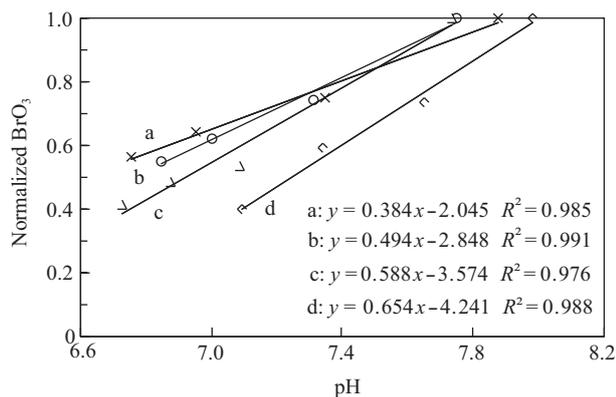


Fig. 4 Relationship between pH and normalized bromate concentration in 4 sets of experiments. Experiments were conducted in 4 different days; characteristics of source water slightly varied; CO₂ dosages varied. Bromate in the CO₂ free case was normalized to 1.0 in each set of experiment. Source water: Br⁻ 215–235 µg/L; NH₄⁺ < 0.02 mg/L-N; pH 8.0–8.3; ozone dosage 5.25 mg/L.

correlation analysis based on all the data above showed an average reduction of 57.1% for a one-unit pH decrease from CO₂ addition.

2.3 Comparison of bromate minimization between acid and CO₂

Effects of CO₂ and acid addition on bromate minimization were compared (Fig. 5). Each set of experiments included: ozonation without pH depression, ozonation with pH lowered to 7.40 ± 0.03 and 6.90 ± 0.03 respectively by adding CO₂, and ozonation with pH lowered to 7.40 ± 0.03 and 6.90 ± 0.03 respectively by adding H₂SO₄. When CO₂ or H₂SO₄ was applied, the dosage was carefully adjusted during ozonation to achieve the designated pH value. Experiments were repeated 6 times on different days under identical operation conditions.

Results showed that at pH 7.4, CO₂ had a slightly lower bromate reduction (4.2%) than did H₂SO₄, with the average bromate formation being 168.8 µg/L and 161.6 µg/L respectively. When pH was further depressed to 6.9, the average bromate formation was 121.8 µg/L and 101.2 µg/L for CO₂ and H₂SO₄, respectively. The acid achieved an 8.8% higher reduction compared to CO₂. This suggests that CO₂ will be suitable for when pH is lowered to a moderate value (7.4 in this study), but less effective than acid when pH is lowered to below 7.0.

The difference in inhibitory effects between CO₂ and acid might be due to the balance between the roles of carbonate, inhibiting the oxidation of bromide to OBr⁻ by scavenging hydroxyl radicals and producing CO₃^{-•} to promote the oxidation of HOBr/OBr⁻. The OH radical concentration decreased when pH was lowered. The ratio of [OH⁻]/[O₃] can be lowered by up to a factor of 10 if the pH is lowered from 8 to 6. When the pH is low, oxidation occurs almost entirely through the direct/indirect pathway (von Gunten, 2003). Therefore, in this case, the indirect pathway is of much less significance, and carbonate plays a lesser role in blocking the indirect pathway. On the other side, the CO₃^{-•} radical is fairly stable (Hofmann, 2000) and will play a greater role at a lower pH than at a higher pH.

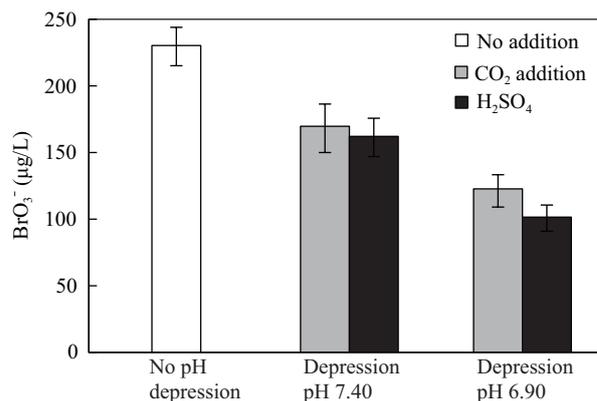


Fig. 5 Bromate minimization by H₂SO₄ and CO₂ additions. Source water: Br⁻ 215–235 µg/L; NH₄⁺ < 0.02 mg/L-N, pH 8.0–8.3; ozone dosage 5.25 mg/L. Data are presented as average of six samples, error bars giving the standard deviation.

2.4 Bromate minimization by CO₂ in the presence of ammonia

Ammonia addition can be an economical way of minimizing bromate formation because even small ammonia concentrations show a positive effect (von Gunten, 2003). In many cases, especially in highly-polluted areas, source water contains ammonia. The impact of CO₂ addition on bromate reduction in the presence of ammonia was investigated and a comparison between CO₂ and H₂SO₄ addition was made. The ammonia dosage was 0.2 mg/L, and the dosage of CO₂ or H₂SO₄ was adjusted to the effluent pH, which was set at 7.40 ± 0.03. Experiments were repeated six times on different days under identical conditions. Results showed that ammonia alone was capable of a 73.9% (range: 66.4%–78.1%) bromate reduction, from 239.4 to 62.5 µg/L, without extra pH depression. Figure 6 shows the pH depression effect on bromate reduction in the presence of ammonia. H₂SO₄ addition caused a reduction of 11.3% (range: 0–19.5%) with an average effluent bromate of 55.3 µg/L, whereas CO₂ addition achieved a higher reduction of 23.5% (range: 18.3%–29.4%) with an average bromate of 46.6 µg/L.

In this study, ammonia inhibited bromate formation with relatively high efficiency by blocking both the direct and direct/indirect pathways and leaving only a little room for pH depression to further block the direct pathway. When CO₂ was applied, not only did it block the direct pathway by pH depression, but also caused the introduction of carbonate to block the indirect pathway that was not affected by ammonia. Therefore, CO₂ addition in the presence of ammonia had a joint inhibitory effect on all three pathways of bromate formation: the blocking of the direct pathway by ammonia and pH depression, the blocking of the direct/indirect pathway by ammonia, and the blocking of the indirect pathway by carbonate. Hofmann and Andrews (2006) proposed a strategy of the joint use of ammonia and carbonate alkalinity to block the three pathways, and their lab-scale experiments showed a 30% to 50% reduction in bromate formation when the alkalinity was increased from 50 mg/L (as CaCO₃) to 119 mg/L under the condition of an excess of ammonia. In source water with a low alkalinity, CO₂ addition together

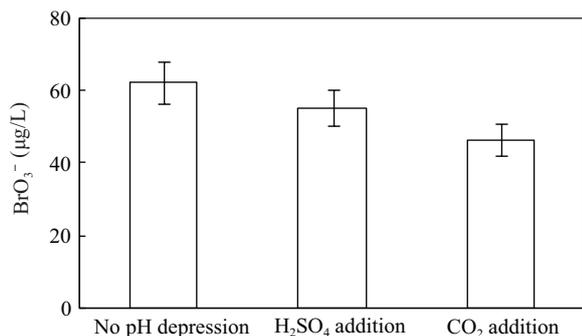


Fig. 6 Bromate minimization by pH depression in the presence of ammonia. Source water: Br⁻. Data are expressed as 215–235 µg/L, NH₄⁺ 0.20 mg/L-N, pH 8.0–8.3; ozone dosage 5.25 mg/L. Data are expressed as average of six samples, error bars giving the standard deviation.

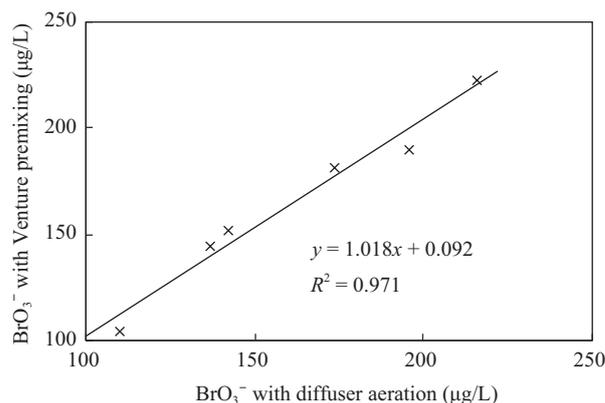


Fig. 7 Impact of CO₂ addition methods. Source water: Br⁻ 215–235 µg/L, NH₄⁺ < 0.02 mg/L-N, pH 8.0–8.3; ozone dosage 5.25 mg/L.

with ammonia will achieve the same result. Nevertheless the bromate could not be completely inhibited for two possible reasons. The first possible reason could be that the incomplete inhibition of bromate was the result of the oxidation of HOBr/OBr⁻ by carbonate radicals. The second reason may be that it was the cause of the remaining of the direct pathway since pH depression and ammonia addition only shifts the equilibrium of OBr⁻ → HOBr so that OBr⁻ still remains but in lowered concentration.

2.5 Impact of CO₂ addition methods

Since the gaseous ozone concentration was slightly diluted when CO₂ was premixed with ozone, this research studied the impact of the dilution of ozone gas on bromate formation. Nitrogen gas corresponding to the maximum CO₂ flow rate was introduced into the ozone gas. Bromate concentration was 212.2 µg/L (with a standard deviation of 8.1 µg/L) without nitrogen, and was 213.3 µg/L (with a standard deviation of 11.8 µg/L) with nitrogen. The results demonstrated no significant impact of the dilution of ozone gas on bromate formation.

The CO₂ was introduced into the column from the diffuser and dissolved into the water along the column when the bubbles rose. The inhibitory effects of CO₂ might not take the full advantages of the total columns due to the gradual dissolution of CO₂. An alternative way was to introduce CO₂ prior to introducing ozone. The efficiency of two CO₂ addition methods were compared, the first being the bubble diffusion method stated above, and the second a premixing method by Venturi. The latter one ensured a complete dissolution of CO₂ before ozonation. In both cases, CO₂ in the off-gas was not detectable, demonstrating a full absorption of CO₂ by water. Figure 7 shows that the two methods made no obvious differences in bromate formation, suggesting that aeration together with ozone without extra equipment installation will be applicable for CO₂ introduction.

3 Conclusions

The pH depression is one of the most feasible methods to minimize bromate formation. This study explored the application of CO₂, a method of pH depression, to inhibit bromate formation for water with a low alkalinity in a

pilot study using a bubble column. Results showed that in the absence of ammonia, carbon dioxide was capable of 38.0%–65.4% bromate reduction for one-unit pH depression. CO₂ had a slightly lower bromate reduction (4.2%) than did H₂SO₄ when the pH was depressed to 7.4, and a more pronounced lower reduction (8.8%) when the pH was depressed to 6.9. In the presence of 0.20 mg/L-N ammonia, bromate was reduced by 73.9%. When the pH was depressed to 7.4, 11.3% of bromate reduction was achieved by H₂SO₄, but its reduction was more than doubled (23.5%) by the introduction of CO₂, demonstrating that the joint use of CO₂ and ammonia is a plausible strategy for blocking all three bromate formation pathways. CO₂ can be applied through the aeration diffuser together with ozone gas without extra equipment installation, resulting in a similar bromate reduction compared with the premixing method through Venturi mixer.

Acknowledgments

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