Formation and minimization of bromate ions within non-thermal-plasma advanced oxidation

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A B S T R A C T
The formation and minimization of bromate ions as a by-product of the operation of a non-thermal plasma reactor for the removal of refractory organic species from drinking water was investigated. BrO₃⁻ formation kinetics was found to be 1st order with respect to the Br⁻ concentration. BrO₃⁻ formation increased when the organic pollutant concentration was elevated by injection of O₃-rich air, generated inside the reactor, back to the water, although measured O₃ concentrations were low (~0.1 mg/l). BrO₃⁻ formation significantly decreased at high temperatures (>35 °C) and low pH (<pH6.0) values and was found insensitive to the carbonate alkalinity concentration. Dosage of hypochlorite followed by ammonia to the inlet water was found to be more effective in minimizing bromate formation than ammonia dosage alone. A general method was developed for assessing the relative importance of the various possible bromate formation pathways within plasma reactors, and a probable dominant BrO₃⁻ formation reaction sequence was suggested for the particular conditions prevailing in non-thermal-plasma systems.

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1. Introduction

Advanced oxidation processes (AOP) are defined as oxidation methodologies based primarily (but not exclusively) upon the oxidation capacity of hydroxyl radicals (OH•) [1]. Non-thermal plasma, an emerging AOP, is formed by applying electric discharge between sets of electrodes. Plasma based treatment reactors are designed to enable OH• formation inside the water or close to the water surface, allowing for efficient contaminants’ oxidation [2]. Corona is a particular non-thermal plasma type, consisting of relatively low-energy electric discharge formed at close to atmospheric pressure in a non-uniform electric field, yielding a large flux of radicals and other reactive molecules [2]. A few works have recently addressed corona water-treatment applications [3–9].

The plasma technology reported in this paper was developed by Aquapure, an Israeli water treatment company. The system applies a combination of high frequency (500 to 1000 Hz) and high voltage (up to 40 kV) pulses, resulting in ionization of ambient air inside the reactor and simultaneous formation of strong oxidizing agents such as ozone, OH• and UV radiation [4,6].

The formation of bromate ions (BrO₃⁻) during strong oxidation of Br⁻ containing water has drawn attention since the definition of bromate as a potential carcinogen by the International Agency for Research on Cancer in 1990. The EPA set the maximum bromate concentration allowed in drinking water at 10 μg/l [10].

Many works have addressed the kinetics and potential mechanisms of bromate ion formation [11–17], predominantly within the context of ozonation processes. The considerably complex bromate formation mechanism in ozonation has been suggested to proceed through reactions combining oxidation of bromide and intermediate species (e.g. HOBr, OBr⁻, Br², BrO³⁻) by either ozone or OH• or a combination thereof [18].

Bromate formation sequence and kinetics depend both upon system operational and water quality parameters, e.g. bromide, carbonate alkalinity and NOM concentrations, pH and temperature [18]. The most promising methods appearing in the literature for minimizing bromate formation in AOP, in general, and ozonation, in particular, are (a) pH reduction [19]; (b) ammonia dosage [18,20,21]; and (c) dosage of Cl₂(aq), followed by ammonia [19].

Available literature on bromate formation and minimization is concerned mainly with bromate formation in ozonation, ozone- and UV/H₂O₂-based AOPs (e.g. [14,19,22]). To the best of our knowledge, no works have addressed the issue of bromate formation in non-thermal-plasma based AOP. The stark difference in conditions, mostly with respect to the dissolved O₃ concentration in plasma-based systems relative to ozonation reactors (1 to 2 orders of magnitude lower in plasma reactors), suggests that the knowledge derived from ozonation systems does not necessarily apply to plasma-based systems.

Accordingly, the objectives of the work were to assess bromate formation potential during non-thermal-plasma water treatment...
operation; to determine the effect of various environmental and operational parameters on bromate formation; to identify and quantify the main pathways for bromate formation; and to assess the efficiency of published methods for minimizing bromate formation within non-thermal plasma operation.

2. Materials and methods

2.1. Experimental system

The experimental system, shown schematically in Fig. 1, consisted of (a) a high voltage (HV) generator, (b) an oxidation reactor comprised of the corona-generating metal and carbon-fiber electrode and the ground stainless steel electrode and (c) an ozone injection unit. Generator characteristics: frequency range 500 to 1000 Hz, maximum voltage 8.0 kV, maximum current 100 A, and rise time of approximately 18 ns.

In the batch experiments the polluted water was pumped from a storage tank to the corona compartment, from which ~30% of the flow returned to the corona compartment and 70% flowed to the ozone injection unit where it was mixed with O3-rich air (~0.1% by weight), which then flowed back to the water tank. Ozone-enriched air was drawn by a venturi-type injector from the reactor headspace, and the O3-rich gas was brought into contact with the water in a static mixer. Injector operation was optional. Main batch operational parameters: (a) solution volume 26 l; (b) recycle flow rate 180–200 l/h; (c) air flow through injector (when operated): 0.5–0.7 m³/h and (d) frequency 500 Hz. In continuous flow experiments the influent was pumped directly into the oxidation reactor and the effluent was drawn out from the water tank. The Hydraulic Retention Time (HRT) in the continuous experiments was set at 20 min by adjusting the inlet stream flow rate, the overall volume in the system remained constant at 26 l also in the continuous experiments.

2.2. Analyses

Bromide and bromate concentrations were analyzed simultaneously by an 881 compact IC pro, Metrohm IC unit. Bromate non-detection was defined as <2.5 µg/L. Phenol and MTBE (methyl tert butyl ether) concentrations were analyzed by an HP 6890 GC unit. Dissolved ozone was measured by the indigo colorimetric method [23]. Absorbance measurements were made using Genesyx 10, spectrophotometer (Spectronics).

2.3. Experimental solution

All experiments were conducted with synthetic solutions. Bromide, Chicago sky blue (CSB), phenol or tert-butanol (in certain cases) was added to distilled water. Inorganic carbon concentration (C_I) was adjusted by sodium bicarbonate; the pH was adjusted with sulfuric acid 0.17 N or NaOH 0.5 N.

3. Results and discussion

3.1. Effect of organic contaminant type and concentration on bromate formation potential

Bromate formation potential was evaluated in continuous experiments as a function of the Br⁻ concentration in the presence of three target organic pollutants (one in each experiment set). Experiments were conducted with 4 mM inorganic carbon concentration (C_I), pH 8.3–8.5 and HRT of 20 min. Inlet CSB (Chicago Sky Blue), phenol and MTBE concentrations were 9.4–10.0, 0.44–0.63 and 0.25–0.32 mg/l, respectively. The O3 injection unit (“injector”) was activated. The BrO₃⁻ concentrations measured in these experiments are shown in Fig. 2 as a function of the Br⁻ concentration. The three inlet organic contaminant molar concentrations were of the same order of magnitude, however, measured effluent concentrations (CSTR conditions) were [4.3–9.0]·10⁻⁷, [1.6–4.1]·10⁻⁸ and [2.1–2.5]·10⁻⁹ M, corresponding to removal efficiencies of 95.3 ± 0.7%, 99.4 ± 0.1% and 28 ± 4%, respectively.

The results in Fig. 2 show that in the presence of phenol and CSB an approximate linear relationship was observed between the formed bromate concentration and the Br⁻ concentration (for 0.5<|Br⁻|<1.9 mg/l), conforming to [12]'s empirical bromate formation equation, derived from batch ozonation experiments at 20°C [18].

The linear relations in Fig. 2 reflect pseudo 1st order kinetics with regard to bromate formation. The pseudo first order constant derived from the experiments with phenol and CSB represent the Br⁻ oxidation potential which includes the potential scavenging of both O₃ and OH⁻ radicals by the organic contaminant present in the water. From the fact that both contaminants' oxidation rates were not affected at all by the Br⁻ concentration (results not shown), it can be concluded that the reaction rate of the oxidants with the organic matter was much higher than their respective oxidation rate of the bromide ions. This conclusion must be restricted to the organic species tested in this work, however, from the fact that Br⁻ oxidation was consistently significantly lower in the presence of the four

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![Figure 1](https://via.placeholder.com/150)  
Fig. 1. Schematic of the experimental plasma system.
organic species tested in the work (CSB, phenol, MTBE and tert-butanol), this observation may be considered representative.

None of the linear approximations in Fig. 2 starts at the origin of axes, suggesting that a minimal bromate concentration is required for bromate to form under the applied experimental conditions. A similar phenomenon was observed by [13] and [22]. Alternatively, [24] suggested that bromate formation followed a lag-phase, related to a buildup of a certain HOBr concentration. Such a phenomenon may explain the observation that, below a certain bromide concentration, bromate did not form at all (at HRT of 20 min). Different bromide concentrations might result in different time lags required for HOBr buildup.

In all the performed experiments the bromate concentration that formed when an organic contaminant was present was significantly lower than the equivalent bromate concentration observed under similar conditions but in the absence of the organic contaminant. For example, for \( [Br^-] = 0.90-0.98 \text{ mg/l} \), \( [BrO_3^-] \) was 5.8 ± 1.9 \text{ mg/l}, 19.9 ± 5.6 \text{ mg/l}, 62.1 ± 5.8 \text{ mg/l} and 120.1 ± 20.8 \text{ mg/l} for experiments with CSB, phenol, MTBE and without an organic contaminant, respectively. When phenol or CSB was present in the water, even at high Br\(^-\) concentrations and low organic matter concentrations, BrO\(_3^-\) formation remained relatively low (below or slightly above the 10 \mu M MCL threshold).

Different BrO\(_3^-\) concentrations formed in the experiments in the presence of the different organic matters tested: CSB, phenol and MTBE. From the fact that low molar phenol concentrations were more effective in suppressing BrO\(_3^-\) generation than higher MTBE molar concentrations it transpires that the minimization of BrO\(_3^-\) formation in the presence of organic matter depends, primarily, upon the reaction rate of the organic matter with ozone, OH radicals and, probably, with HOBr and OBr\(^-\) as well. [25] reported that the mechanism for the decrease in bromate formation in ozonation processes in the presence of NOM stems from direct reaction between NOM and ozone or NOM and hydroxyl radicals and a reaction between NOM and bromine, which is the main intermediate in the bromate formation reaction sequence [25]. The rate constants of the reactions of MTBE and phenol with ozone were reported to be 0.14 and 1.8 · 10\(^2\) \text{ M}^{-1} \text{ s}^{-1} \text{/(M s)}, respectively [26,27] and of MTBE and phenol with hydroxyl radicals 1.9 · 10^{-9} and 1.4 · 10^{-10} \text{ M}^{-1} \text{ s}^{-1} \text{/(M s)}, respectively [27,28]. Thus, the rates at which phenol reacts with ozone and hydroxyl radicals are higher than the respective MTBE rates, however, the difference is much higher with regard to the reaction with ozone. Moreover, the reaction rate of phenol with hypobromous acid is relatively fast (2.2 · 10\(^8\) \text{ M}^{-1} \text{ s}^{-1})[29]) and it can be consequently deduced that the reaction rate of MTBE with hypobromous acid is relatively slow since HOBr, similarly to ozone, is known to react rapidly mostly with compounds containing double bonds or aromatic rings [14]. These data support the claim that higher reaction rates of the organic matter with O\(_3\) and HOBrOBr\(^-\) act to reduce the bromate formation rate, but it is still unclear which of the two reactions dominates. Due to the high reaction rate constants of both phenol and MTBE oxidation by OH\(^+\), it can be reasonably assumed that these reactions play a less important role in determining the difference between bromate minimization effects of the two contaminants.

The effect that the type of the organic matter has on bromate formation was further illuminated using two types of organic species, phenol and CSB, oxidized under batch conditions. In both cases a similar behavior was observed. Bromate formation, at a given hydraulic retention time, was higher when the organic matter concentrations were lower. Furthermore, in both cases a threshold organic concentration was identified, above which no bromate was detected at all.

Fig. 3 presents the results of bromate formation versus time in batch experiments conducted with two initial phenol concentrations: 1.8—1.9 \text{ mg/l} and 5.5—5.7 \text{ mg/l}. Clearly, bromate formation was higher at the low phenol concentrations. Moreover, bromate started to form only when the phenol concentration dropped below ~0.7 \text{ mg/l}. In similar experiments, performed with different concentrations of CSB, bromate formation started only when the CSB concentration dropped below 1.0 \text{ mg/l}. These results corroborate previous observations that below certain oxidant concentration, bromate formation is very low to negligible. [11] reported a threshold ozone concentration, which depended on the DOC concentration in water, below which no BrO\(_3^-\) formed. The results of the current work support the observed dependence between bromate formation and the DOC concentration.

3.2. Assessing the relative importance of various bromate formation pathways in the investigated plasma system

The mechanism of bromate formation is described in the literature as a combination of oxidation of bromide by ozone and/or hydroxyl radicals. Quantifying the relative pathways through which bromate is formed in a given operational scenario is imperative for deciding on the most appropriate bromate minimization strategy.

To this end, a general methodology was developed for approximating the relative importance of the different bromate formation pathways. It is emphasized that different operational conditions (batch vs. continuous operation or injector operated vs. disconnected),
as well as different water qualities (C₇, temperature, type and concentration of organic contaminants) will necessarily affect the relative importance of the various bromate formation pathways. However, in order to exemplify the developed methodology it was chosen to differentiate between bromate formation pathways in a system operated in the absence of organic contaminant, i.e. under conditions where bromate formation was maximized.

Tert-butanol, an efficient radical scavenger (reacts with hydroxyl radicals to generate inert intermediates, thereby terminating the radical reaction chain) serves as an inhibitor of radical reactions and for distinguishing between O₃ and OH⁺-based reactions [30]. It reacts very rapidly with hydroxyl radicals (K_{TB-OH} = 5 \cdot 10^{8} \text{M}^{-1} \text{s}^{-1}) whereas its reaction rate with ozone is 11 orders of magnitude slower (K_{TB-O3} = 3 \cdot 10^{-3} \text{M}^{-1} \text{s}^{-1}) [30].

[12] proposed three main bromate formation pathways, two of which consist of combined ozone and hydroxyl radical reactions. In contrast, [15] insisted that bromate formation in AOP is governed solely by OH⁺ induced reactions. However, since dissolved ozone in water is known to react to generate hydroxyl radicals [2], the two approaches are not necessarily contradicting.

Adapting the definitions of [12] in plasma reactors, three main bromate formation pathways may be postulated to occur: (a) Pure ozone-based reactions, (b) Pure radical reactions and (c) combined ozone and radical reactions. Bromate forming due to pure ozone-based reactions may be quantified from experiments carried out in the presence of tert-butanol, which may be assumed to practically scavenge all the hydroxyl radicals' concentration. Bromate formed in the pure radical based reactions, i.e. bromate that forms mainly through hydroxyl radicals, can be isolated from results of experiments conducted with the injector turned off, in which the dissolved ozone concentration was much lower than in experiments conducted with activated injector, thus it can be assumed that the bromate forms mostly through radical reactions. The potential bromate formation was considered, with this approach, as the concentration that formed in experiments conducted with no tert-butanol addition and with activated injector. Under such conditions bromate is formed through reactions with ozone, hydroxyl radicals and a combination thereof. Batch experiments conducted in the presence of tert-butanol and in the absence of organic contaminant showed zero bromate formation when the injector was disconnected, indicating that bromate formation depended strictly upon the presence of either ozone or hydroxyl radicals. Under the “combined ozone and radical reaction sequence” bromate formation proceeds through a pathway involving both ozone and hydroxyl radical oxidation routes. The fraction of bromate which forms through this pathway can be estimated by subtracting the sum of bromate formed in the pure ozone and the pure radical pathways from the potential bromate formation.

Using the technique described above, the weights of the different bromate formation pathways were analyzed in continuous experiments in the absence of organic matter. The results showed that ~6.5% of the bromate formed through the pure ozone pathway, ~4.0% via the pure radical pathway and as much as ~89.5% through the combined pathway. Note that these approximations hold true for the specific conditions tested, i.e. in the absence of an organic contaminant. Once an organic species which reacts rapidly with either O₃ or OH⁺ radicals (or with both) is present, pathway distribution may change considerably. However, the described approximation technique may be implemented to determine the weights of the different bromate formation pathways under any experimental conditions.

3.3. Effect of water quality and operational parameters on bromate formation

3.3.1. Injector operation

The effect of injector operation on bromate formation was assessed in both batch and continuous experiments in the absence and in the presence of CSB, and in continuous experiments with MTBE.

In the continuous experiments conducted with CSB (10.11± 0.08 mg/l), MTBE (0.30± 0.04 mg/l) and no organic contaminant the bromate concentration that formed when the injector was inactivated was 26%, 6% and 4%, respectively, of the bromate that formed when the injector was activated (other operational conditions being similar). With the injector inactive, the bromate concentration that formed during all of the continuous experiments was very low: even in the absence of an organic contaminant the formed bromate concentration was as low as 4.7± 0.7 μg/l (bromide and C₇ concentrations 0.93–1.03 mg/l and 4 mM, respectively, temperature 19–26 °C. MTBE and CSB removal were 28± 4% and 95± 1% with the injector activated compared to 25± 5% and 68± 1% with the injector inactivated).

It is widely accepted (e.g. [12,18–20,22,24]) that the formation of bromate via the various formation pathways depends upon the individual and combined O₃ and OH⁺ concentrations. The relative weight of each formation pathway and the factors affecting it are, to date, not entirely understood. In parallel, the kinetics of the degradation of the organic contaminant is also a function of the O₃ and OH⁺ oxidation potentials, however, not necessarily at the same proportion. Since it has been shown that turning the injector off significantly reduces the potential for bromate formation, this action should be considered a bromate minimization strategy. However, this should be considered only in case the target contaminant is significantly less sensitive to ozone oxidation than Br⁻ is.

3.3.2. Effect of inorganic carbon concentration (C₇)

The effect of C₇ on bromate formation was tested in batch experiments with 1.7 mg/l initial bromide concentration, 0.9 mg/l initial CSB concentration and activated injector. Bromate formation was measured with C₇ = 4 and 0.6 mM.

Bicarbonate/carbonate species have the capacity to scavenge HO⁺ radicals by reacting with them to form carbonate radicals, which have the potential to promote Br⁻ oxidation [18]. In addition, increasing carbonate alkalinity was used to promote the ozone stability [11]. By scavenging OH⁺ radicals carbonate ions decrease ozone consumption, thus higher ozone levels have been reported upon the addition of alkaline CT species in ozonation processes [13]. Indeed, in the context of ozonation most works report that higher C₇ promotes bromate formation [11,13,18], although the opposite has also been observed [22].

In the current work no significant difference was observed in both bromate formation and CSB degradation rates between the two C₇ concentrations (results not shown).

The fact that the results differed from those reported for ozonation systems emanates, in all likelihood, from the inherently different OH⁺ concentrations in both systems. The background OH⁺ concentration in plasma systems is significantly higher and, therefore, the small fraction scavenged by the higher C₇ concentration may be considered negligible, whereas in ozonation systems the typical OH⁺ concentration is much lower, making this phenomenon much more significant. Moreover, the effect of C₇ on the ozone concentration is also expected to be very small in plasma systems because of the inherently low ozone concentration, approximately two orders of magnitude lower than in typical ozone applications.

3.3.3. Effect of pH

The direct effect of the pH value on bromate formation was tested in batch experiments with initial bromide and CSB concentrations of 1.7 and 9.0 mg/l at two different pH ranges: (1) 6.0–6.1 (C₇ = 0.5 mM) and (2) 8.2–8.4 (C₇ = 4 mM). The effect of the pH value was examined with the injector both activated and disconnected. No attempt was made to maintain C₇ constant in these experiments since it has been shown to have no effect on bromate formation (Section 3.3.2). Bromate formation was found to be affected by the pH value only
when the injector was activated: at pH –6.0 the formed bromate concentration was around 50% of the respective value attained at pH –8.3 after 90 min of batch operation. Conversely, with the injector disconnected, identical (and very low) bromate formation was attained at the low and high pH values.

These results can be explained as follows: a known and significant bromate formation pathway proceeds through the oxidation of HOB\(_\text{r}\)O\(_\text{Br}\) by hydroxyl radicals to form BrO\(_\text{3}\). The rate of O\(_\text{Br}\)\(^-\) and HOB\(_\text{r}\)O\(_\text{Br}\) oxidation to BrO\(_\text{3}\) by OH\(_\cdot\) has been reported to be 4.5 \cdot 10^9 and 2 \cdot 10^9 \text{1/(M·s)}, respectively [12]. The pH value determines the equilibrium between hypobromous acid and hypobromite (HOB\(_\text{r}\) → O\(_\text{Br}\)\(^-\) + H\(^+\); \(pK_a = 8.86\) at 20 °C). Lower O\(_\text{Br}\)\(^-\) concentration (i.e. lower pH) is thus expected to slow down the rate of bromate formation by slowing down the formation rate of BrO\(_3\). On the other hand, when the injector is disconnected, bromate formation is lower because the formation of HOB\(_\text{r}\)O\(_\text{Br}\), which is a function of the O\(_\text{3(aq)}\) concentration, slows down, rendering the effect of low pH less pronounced.

HOB\(_\text{r}\) and O\(_\text{Br}\)\(^-\) have been reported to have different reaction rates with ozone [18]. However, since, in the current work, it was observed that HOB\(_\text{r}\)O\(_\text{Br}\)\(^-\) reacts mainly with hydroxyl radicals (Section 3.5), the effect of the different reaction rates with ozone on bromate formation was assumed negligible.

### 3.3.4. Effect of temperature

The effect of temperature on bromate formation was tested in a set of batch experiments operated with and without organic contaminant (CSB), with bromide concentration of 0.9 mg/l and \(C_T = 4 \text{ mM}\). The first three experiments were conducted with the injector disconnected, no organic contaminant present and three temperature ranges: 34.6 ± 0.5 °C, 20.6 ± 2.3 °C and 12.7 ± 0.7 °C, and corresponding initial phenol concentrations of 0.22 ± 0.16 mg/l. The average effluent phenol concentration was 0.16 ± 0.11 mg/l and average MTBE removal percentage was 29 ± 6%.

### 3.4. Minimizing bromate formation within plasma reactor operation

The effect of chlorine and ammonia addition on bromate formation was investigated in continuous experiments under varying water quality and experimental conditions, as summarized in Table 1. All phenol experiments listed in Table 1 were conducted with an average initial phenol concentration of 0.515 ± 0.079 mg/l. The effluent phenol concentrations were in all cases lower than 0.005 mg/l. All the experiments with MTBE were conducted with initial concentration of 0.22 ± 0.16 mg/l. The average effluent MTBE concentrations were 0.16 ± 0.11 mg/l and average MTBE removal percentage was 29 ± 6%.

#### 3.4.1. Bromate minimization by ammonia dosage

Minimization of bromate formation by ammonia addition has been proposed to occur via reaction with HOB\(_\text{r}\) (or O\(_\text{Br}\)\(^-\)) as shown in Eq. (1), which reduces the availability of these species for participating in bromate formation reactions [20].

\[
\text{HOBr} + \text{NH}_3 \rightarrow \text{NH}_2\text{Br} + \text{H}_2\text{O} \quad K = 7.5 \cdot 10^{17} \text{L/(M·s)}
\]

Table 1 (Exp. #2) shows the bromate concentration attained in experiments conducted with various pH values and ammonia concentrations of 0.1 mg N/l in the absence of organic contaminant. As evident in Table 1, a significant reduction in bromate formation was attained, down to concentrations lower than the 10 µg/l threshold, by the addition of ammonia concentration as low as 0.1 mg N/l (96.4%
average reduction in the bromate concentration, relative to a similar experiment in which no ammonia was added) at the pH range 8.4–8.6. Experiments aimed at determining the threshold ammonia concentration above which bromate concentration in the outlet stream would be <10 μg/l showed (1) that higher ammonia concentration did not further reduce bromate formation and (2) that lower ammonia concentrations could not bring the bromate concentration down to the required 10 μg/l threshold (results not shown). Under similar conditions, but at pH 7.6 and pH 7.2 (Exps. #3 and #4) the resulting bromate concentration was approximately similar. In experiments conducted with MTBE as the organic contaminant (Exps. #5 through #7 in Table 1), at both pH 8.3 and pH 7.1 the addition of ammonia also resulted in bromate formation to below 10 μg/l. The fact that low pH did inhibit the ammonia effect on bromate formation contradicted the results of [13] and [18], who reported the opposite within the context of ozonation processes [13,18].

From Exps. #1 through #7 in Table 1 it can be concluded that in the absence of organic matter or when MTBE is present in the water, addition of a low ammonia concentration (0.1 mgN/l) is sufficient for minimizing bromate formation.

However, in experiments conducted with phenol as the organic contaminant ammonia addition was shown to minimize bromate formation only at pH 8.3–8.5 but not at lower pH values (Exps. #8 to #12). In contrast with the excellent bromate inhibition results obtained in the absence of organic matter and with MTBE, in these experiments the average percentage of bromate formation inhibition by the ammonia dosage did not exceed 64.3% and the residual bromate concentration was relatively high (16.8 ± 1.1 and 11.8 ± 2.4 μg/l in experiments conducted with 1.98 and 0.97–0.98 mg/l [Br−], respectively). The trend apparent from these results already appears in the literature, e.g. [13] showed that an addition of 1 mg NH4-N/l in experiments conducted with pH ranging from 8.2 to 8.7 did inhibit the ammonia effect on bromate formation.

The in situ reaction of HOBr with unsaturated organic compounds is relatively high (2.2 · 106 1/(M·s), [28]). On the other hand, MTBE does not contain double bonds or aromatic rings and therefore can be assumed to have a lower reaction rate with hypobromous acid, allowing for a higher camouflaging efficiency of HOBr by ammonia.

The reduction in bromate formation by ammonia addition was suggested to occur via Eq. (1) followed by Eq. (2) [19]:

\[
\text{Br}^- + \text{HOCI} \rightarrow \text{HOBr} + \text{Cl}^- \quad K = 1550 \ (1/(M\cdot s)).
\]

Exps. #13 and #14 in Table 1 show the results of combined chlorine and ammonia dosage experiments. HOCl was dosed to the inlet solution which was then stirred for 5 min in order to enable the reaction between chlorine and bromide to occur. Subsequently, ammonia was dosed.

Table 1 (Exps. #13 and #14) shows that the combination of chlorine and ammonia dosages minimized bromate formation considerably to below the 10 μg/l MCL threshold, regardless of pH. It is possible that a lower dosage of chemicals can also prevent bromate formation, however assuming chloramination is practiced downstream, the relatively high ammonia concentrations were not considered problematic.

Following chlorine addition, a lower bromide ion concentration was measured. In Exps. #13 and #14 the Br− concentration after chlorine addition was 0.53 ± 0.04 and 0.71 ± 0.06 mg/l, and at the outlet of the reactor 0.83 ± 0.02 and 0.79 ± 0.12 mg/l, respectively. These observations support the mechanism suggested by [19] for bromate minimization by combined chlorine and ammonia dosages. Early addition of chlorine (prior to introduction of the water into the plasma reactor) to the solution acts to minimize the free bromide ion available for bromate formation via the radical pathways.

No change in the phenol degradation rate was observed in the chlorine/ammonia dosage experiments. In all the experiments with phenol, its initial concentration was 0.41–0.64 mg/l, and the phenol in the outlet stream was lower than 0.005 mg/l. However, a certain decrease in the phenol concentration was observed prior to the introduction into the plasma reactor, following the chlorine dosage stage.

3.5. Proposed main mechanism of bromate formation in non thermal plasma

An attempt was made to identify the main bromate formation pathway in the investigated plasma reactor. Based on the results obtained in this work a likely dominant pathway should conform to the following four observations: (1) since bromate formation was minimal both when the injector was disconnected and when the temperature was high it is likely that Br− is predominantly oxidized by O3 rather than by OH•; (2) Since the addition of ammonia clearly inhibited bromate formation, it follows that bromate is mainly formed through pathways which include the intermediates HOBr and OBr−; (3) it was observed that most of the bromate is formed through the combined oxidation pathway; (4) A mass balance performed round Br− containing species closed better when the injector was disconnected, indicating a much lower HOBr and OBr− accumulation when the ozone concentration was lower. Br mass recovery was calculated as the percentage of the sum of measured effluent Br− and BrO3− concentrations out of the known influent Br− concentration. A difference from theoretical 100% recovery was attributed to HOBr and OBr− accumulation. For example, in continuous experiments conducted (a) with no organic contaminant and (b) in the presence of MTBE, the Br mass recovery was relatively low: 92.2 ± 3.4 and 97.8 ± 0.8 when the injector was operated and 99.5 ± 0.8 and 99.8 ± 0.05 when the injector was disconnected, respectively. Similar conclusions (results not shown) were drawn from experiments conducted with t-butanol, azo and phenol.

Combining the four observations above the following (prevailing) pathway sequence is proposed: The first stage involves reaction between Br− and ozone, which leads to the formation of HOBr/OBr−...
(Eqs. 3 and 4). Next, HOBr/BrO\(^{-}\) reacts with hydroxyl radicals to form BrO\(^{•}\) (Eqs. 5 and 6). Subsequently, BrO\(^{•}\) reacts with H\(_2\)O to form BrO\(_2\)\(^{-}\) (Eq. 7), which further reacts with ozone or hydroxyl radicals to form bromate (Eqs. 8, 9 and 12 or 10). The proposed dominant reaction pathway appears as a thickened line in Fig. 4, on top of the reaction pathway alternatives chart proposed by [14], on which additional reactions proposed by [24] were combined.

\[
\begin{align*}
\text{O}_3 + \text{Br} & \rightarrow \text{HOBr} + \text{O}_2 \quad k = 160 \pm 20 \text{ I}/(\text{M} \cdot \text{s}) \quad (3) \\
\text{BrO}^- + \text{H}^+ & \rightarrow \text{HOBr} \quad \text{pK}_a = 8.86 \text{ at } 20 \text{ °C} \quad (4) \\
\text{BrO}^- + \text{OH}^• & \rightarrow \text{BrO}^• + \text{OH}^- \quad k = 4.5 \cdot 10^9 \text{ I}/(\text{M} \cdot \text{s}) \quad (5) \\
\text{HOBr} + \text{OH}^• & \rightarrow \text{BrO}^• + \text{H}_2\text{O} \quad k = 2 \cdot 10^9 \text{ I}/(\text{M} \cdot \text{s}) \quad (6) \\
\text{BrO}^• + \text{BrO}^• + \text{H}_2\text{O} & \rightarrow \text{BrO}_2^- + \text{BrO}^- + 2\text{H}^+ \quad k = 4 \cdot 10^9 \text{ I}/(\text{M} \cdot \text{s}) \quad (7) \\
\text{O}_3 + \text{BrO}_2^- & \rightarrow \text{BrO}_3^- + \text{O}_2 \quad k = 10^3 \text{I}/(\text{M} \cdot \text{s}) \quad (8) \\
\text{BrO}_2^- + \text{OH}^• & \rightarrow \text{BrO}_2^• + \text{OH}^- \quad k = 1.9 \cdot 10^9 \text{ I}/(\text{M} \cdot \text{s}) \quad (9) \\
\text{BrO}_2^• + \text{BrO}_2^• & \rightarrow \text{Br}_2\text{O}_4 \quad k = 1.4 \cdot 10^9 \text{ I}/(\text{M} \cdot \text{s}) \quad (10) \\
\text{Br}_2\text{O}_4 + \text{OH}^- & \rightarrow \text{BrO}_3^- + \text{BrO}_2^- + \text{H}^+ \quad k = 7 \cdot 10^8 \text{ I}/(\text{M} \cdot \text{s}) \quad (11) \\
\text{OH}^• + \text{BrO}_2^- & \rightarrow \text{BrO}_3^- + \text{H}^+ \quad k = 2 \cdot 10^9 \text{ I}/(\text{M} \cdot \text{s}) \quad (12)
\end{align*}
\]

The extent of BrO\(_3\) formation in the investigated plasma reactor depended mainly upon the Br\(^{-}\) concentration (1st order kinetics), the composition of the background dissolved organic matter in the treated water and the required final concentration of the contaminant in the effluent. The extent of BrO\(_3\) formation was affected by the pH and temperature of the treated water and not affected by the inorganic carbon concentration.

- **4. Conclusions**
  - **BrO\(_3\)** formation in the investigated plasma reactor depended mainly upon the Br\(^{-}\) concentration (1st order kinetics), the composition of the background dissolved organic matter in the treated water and the required final concentration of the contaminant in the effluent.
  - All the organic species tested in the work showed higher reaction rates than Br\(^{-}\) with both the ozone and the OH\(^•\) generated in the plasma reactor. Consequently, for each organic species a threshold concentration was observed, above which bromate formation was very low to negligible, due to efficient scavenging of the oxidants by the organic matter.
  - **BrO\(_3\)** formation under the conditions prevailing in plasma systems can be effectively minimized by stepwise addition of low concentrations of hypochlorite and ammonia.
  - The dominant bromate formation pathway in plasma reactors proceeds through Br\(^{-}\) oxidation by O\(_3\) to HOBr/BrO\(^{-}\), followed by HOBr/BrO\(^{-}\) oxidation by OH\(^•\) to BrO\(^•\), which further hydrolyzes to...
BrO$_2^-$, which in turn can be oxidized by either OH• and O$_3$ to form bromate.

References


