

Review

Advances in Treatment of Brominated Hydrocarbons by Heterogeneous Catalytic Ozonation and Bromate Minimization

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Abstract: The formation of carcinogenic bromate ions is a constraint when ozone is used for the remediation of water containing brominated organic materials. With its strong oxidizing ability, ozone rapidly transforms bromide in aqueous media to bromate, through a series of reactions involving hydroxyl radicals. Several strategies, such as limiting the ozone concentration, maintaining pH < 6, or the use of ammonia or hydrogen peroxide were explored to minimize bromate generation. However, most of the above strategies had a negative effect on the ozonation efficiency. The advanced oxidation processes, using catalysts together with ozone, have proven to be a promising technology for the degradation of pollutants in wastewater, but very few studies have been conducted to find ways to minimize bromate formation during this approach. The proposed article, therefore, presents a comprehensive review on recent advances in bromate reduction in water by catalytic ozonation and proposes reaction mechanisms associated with the catalytic process. The main aim is to highlight any gaps in the reported studies, thus creating a platform for future research and a quest to find environment friendly and efficacious catalysts for minimizing bromate formation in aqueous media during ozonation of brominated organic compounds.

Keywords: bromate minimization; catalytic ozonation; metal oxides; bromide

1. Introduction

The need to reduce environmental pollution is currently receiving urgent attention around the world. The rapid increase in the human population, coupled with growing demands from industrial and other sectors, has triggered the large-scale usage of diverse non-biodegradable chemicals, leading to extensive pollution of water systems. Since these polluted waters pose a serious threat to the environment, ongoing research is conducted to explore cost effective treatment methodologies for the removal of varied toxic chemicals from the water systems. An alternative to chlorination and adsorption agents for water purification is ozonation, which is becoming a useful methodology for improving the quality of water. The use of ozone has proven to be excellent for microorganism destruction and biological contaminant removal from water [1], but is not effective for degrading recalcitrant organic pollutants in water. The presence of bromide (Br^-) in polluted waters poses a serious problem during ozonation. Bromide is rapidly oxidized to toxic bromate (BrO_3^-) during ozone treatment. Bromide is usually present in low concentrations of between 10^4 and 10^6 ppb in wastewaters and approximately 67×10^3 ppb in seawater [2]. Relatively low amounts were found in rainwater, ranging from 0 to 110 ppb [3], but in groundwater, between 10 and 2×10^3 ppb were detected [4]. Higher bromide

concentrations have been reported in waters and soil samples near oceans [5]. Mining and leaded petrol [6], fertilizers and insecticides are considered major sources of bromine contamination of the environment and aquatic systems [7]. Bromide was also found in many treated water facilities ranging from 3000 to 10,000 ppb [8,9]. If bromide levels as low as 20 ppm are present in water during ozonation, the potential exists for bromate formation to occur through a combination of ozone and hydroxyl radical reactions [1]. Bromate is a known human carcinogen [10–12] and its maximum allowable limit in drinking water is set at 10 ppb or lower [13]. Therefore, it is crucial to minimize or prevent its formation in drinking water.

In aqueous systems, ozone oxidizes bromide to bromate via three different pathways [14]. The dominance of a particular pathway is dependent on the amount of bromide, organic carbon and pH of the substrate solution. As illustrated in Figure 1, the first pathway (direct pathway) is initiated by the reaction of bromide ion with molecular ozone to form OBr^-/HOBr . The OBr^- is further oxidized by dissolved O_3 to BrO_2^- and finally to BrO_3^- . The second pathway (direct/indirect pathway) is facilitated by the molecular ozone, resulting in the formation of OBr^-/HOBr . However, in this route the formed OBr^- is oxidized by HO^\bullet radicals to a series of highly reactive oxygenated radicals. Further ozonation produces BrO_3^- ions. According to Richardson et al. [15], this pathway is favoured if solution pH and alkalinity of the water is high. In the third pathway, the HO^\bullet radicals interact with bromide ions resulting in the generation of BrO^\bullet radicals, which is disproportionate to bromite ions. The bromite ions are then oxidized by molecular ozone to produce bromate ions.

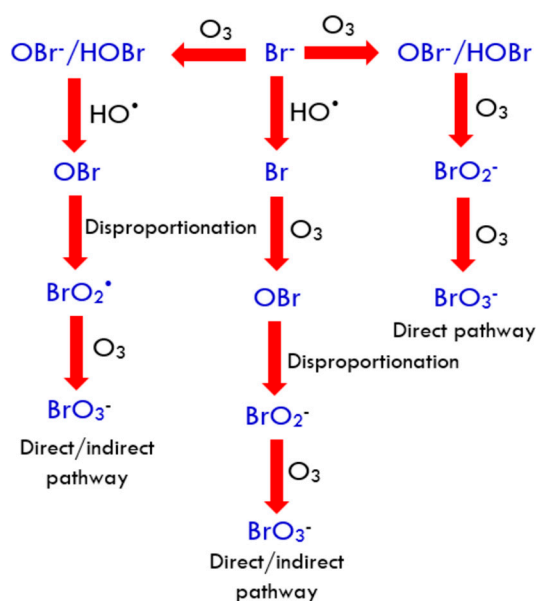
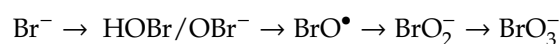


Figure 1. Bromate formation pathways [14].

The use of suitable heterogeneous catalysts has proven to be beneficial to enhance the efficiency of the ozonation process and minimize the generation of toxic by-products [16]. Studies have shown that hydroxyl radicals generated during ozonation in the presence of metal oxides could increase bromate formation [17]. This review presents a comprehensive assessment on recent advances on bromate reduction in water by heterogeneous catalytic ozonation.

2. Bromate Minimization Strategies

The following mechanism was proposed by von Gunten and Hoigne' for the conversion of Br^- to BrO_3^- during ozonation [18]:



They concluded that the direct oxidative conversion of Br^- to HOBr/OBr^- was mainly controlled by molecular ozone, while further oxidation of HOBr/OBr^- to BrO^\bullet radicals was influenced by HO^\bullet radicals. The unstable BrO^\bullet radicals disproportionate to BrO_2^- . The dissolved ozone in the water then rapidly oxidizes BrO_2^- to BrO_3^- [1]. Limited studies have been conducted to establish the effects of catalytic ozonation on bromate formation. The most recent studies are discussed below.

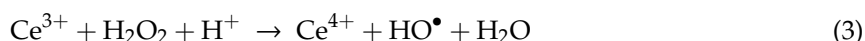
2.1. MCM-48, CeO_2 and $\text{Ce}_x\text{-MCM-48}$

Li et al. [19] reported on catalytic ozonation of bromide containing waters with MCM-48, CeO_2 and combined mesoporous sieve $\text{Ce}_x\text{-MCM-48}$ (cerium combined with MCM-48) with various Si/Ce molar ratios ($\text{Ce}_{30/66/100/200}\text{-MCM-48}$). All catalysts were able to considerably impede BrO_3^- formation in comparison to ozonation alone. After 30 min of ozone treatment, the inhibition efficiencies of MCM-48 and CeO_2 were 78.6% and 63.9%, respectively. When MCM-48 was doped with Ce, a marked improvement in BrO_3^- minimization was observed. When the Ce content was increased from $x = 200$ to $x = 66$, BrO_3^- yield decreased, giving a maximum inhibition efficiency of 91% after 30 min of ozonation. However, an additional increase of Ce to $x = 30$, resulted in an increase in BrO_3^- concentration and an inhibition efficiency of 78%. Their explanation for this trend was that doping MCM-48 with Ce resulted in the generation of more surface hydroxyl groups, which successively enhanced decomposition of O_3 on the active sites of the catalyst surface. However, doping beyond $x = 66$ blocked the active sites, leading to a destruction of the mesoporous structure of MCM-48, hence leading to poor catalyst activity.

Li et al. [19] proposed a bromate reduction pathway for $\text{Ce}_{66}\text{-MCM-48}$ with the aid of bromine mass balance studies. Their results revealed that $\text{Ce}_{66}\text{-MCM-48}$ did not adsorb Br^- , HOBr/OBr^- and BrO_3^- , the main bromine-containing species present in the water solution. The amounts of both HOBr/OBr^- and BrO_3^- in $\text{Ce}_{66}\text{-MCM-48}$ ozonation were expressively lower, relative to ozone in absence of catalyst, while the amount of Br^- was much higher in $\text{Ce}_{66}\text{-MCM-48}$ ozonation. As the bromide oxidation is primarily controlled by O_3 , $\text{Ce}_{66}\text{-MCM-48}$ ozonation tends to prevent BrO_3^- production by limiting the influence of direct O_3 oxidation. The results have shown that O_3 decomposed faster with $\text{Ce}_{66}\text{-MCM-48}$ (82% decomposition after 5 min), in comparison to ozonation alone (53% decomposition in the first 5 min). Since a lower amount of dissolved O_3 exists in $\text{Ce}_{66}\text{-MCM-48}$ ozonation, the consecutive oxidation reactions from $\text{Br}^- \rightarrow \text{HOBr}/\text{OBr}^- \rightarrow \text{BrO}_3^-$ are all inhibited. The generated secondary oxidant, HO^\bullet , reacts with some bromine containing species, organic micropollutants, or combine to form H_2O_2 . The results showed that H_2O_2 concentration steadily increases during ozonation alone, reaching a maximum value of $0.6 \mu\text{M}$ after 20 min. With ozonation in the presence of $\text{Ce}_{66}\text{-MCM-48}$, a higher H_2O_2 concentration was detected, but it remained constant ($1.5\text{--}1.7 \mu\text{M}$) for the entire 20 min. Another bromate inhibition mechanism involved electron transfer reactions between Ce^{3+} and Ce^{4+} on $\text{Ce}_{66}\text{-MCM-48}$ surface. These reactions lead to the inhibition of Br^- to HOBr/OBr^- , thus resulting in lower BrO_3^- formation. The Ce^{3+} surface ions underwent oxidation by Br^\bullet and BrO^\bullet to form Ce^{4+} [20] according to the following pathway:



Ce^{3+} also reacts with H_2O_2 to form Ce^{4+} [21]:

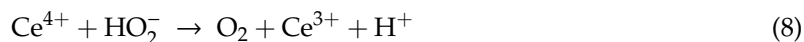


An alternative pathway produces H_2O_2 from aqueous O_3 decomposition





Ce^{3+} is regenerated by HO_2^- , which converts Ce^{4+} to Ce^{3+} [21]:



2.2. α -FeOOH, α -Fe₂O₃, γ -FeOOH and CeO₂

T. Zang et al. [22] investigated the effect of a number of metal oxides, such as α -FeOOH, α -Fe₂O₃, γ -FeOOH and CeO₂, on bromate production during ozone treatment of bromide in water. The catalytic reactions with α -Fe₂O₃ produced more BrO₃⁻ relative to ozonation alone, whereas the reactions with α -FeOOH, γ -FeOOH and CeO₂ minimized bromate formation. However, CeO₂ was most active in reducing bromate production. They determined simultaneously the concentrations of Br⁻ and HOBr/OBr⁻ for uncatalysed ozonation and CeO₂ catalysed ozonation. They found that the Br⁻ amounts in catalytic ozonation was lower with ozone treatment alone before 15 min, and remained similar thereafter. The HOBr/OBr⁻ amount in CeO₂ catalytic ozonation was always significantly higher in comparison to ozone treatment alone. According to von Gunten [1], HOBr/OBr⁻ is an essential intermediary for BrO₃⁻ production during ozonation, therefore, its accumulation in CeO₂ catalytic ozonation suggests that CeO₂ considerably inhibits the conversion of HOBr/OBr⁻ to BrO₃⁻.

The formation of H₂O₂ was detected in both ozonation alone and ozonation with CeO₂. The results showed that the amount of H₂O₂ with CeO₂ was poorer compared to single ozonation. Studies have shown that the surface of CeO₂ can initiate the decomposition H₂O₂ generating oxygen in water [23]. Therefore, the lesser H₂O₂ amount in CeO₂ catalytic ozonation can be attributed to its concurrent disintegration on the surface of CeO₂. One study mentioned that low amounts of hydrogen peroxide can promote BrO₃⁻ formation, arising from hydroxyl radical formation from the interaction of HO₂⁻ with O₃ [1], and other studies discussed that hydrogen peroxide at high amounts (H₂O₂/O₃ molar ratio >1:2) is likely to reduce HOBr/OBr⁻ to Br⁻, hence minimizing BrO₃⁻ formation [17,18,24]. According to Zang et al. [22], the enhanced BrO₃⁻ minimization in CeO₂ catalytic ozonation is primarily due to the lower H₂O₂ amounts. Since CeO₂ catalytic ozonation produced a lower amount of H₂O₂ than single ozonation, the HO[•] amount is expected to be moderately lower, hence resulting in a lower oxidation rate of HOBr/OBr⁻ to BrO[•]. Furthermore, BrO[•] can be reduced to HOBr/OBr⁻ by Ce³⁺, which is a temporary reductive state of surface Ce⁴⁺ in catalytic decomposition of H₂O₂ [25]. Thus, an additional pathway for BrO₃⁻ minimization is the reduction of BrO[•] to HOBr/OBr⁻ on the CeO₂ surface. Both BrO₃⁻ reduction routes require the involvement of surface active Ce⁴⁺ sites.

It has been reported that SO₄²⁻ ions, when combined with metal oxides, have a strong attraction for their surface sites [26]. Zang et al. [22], therefore, added various concentrations of SO₄²⁻ to the bromide containing solutions to ascertain its affinity for surface active Ce⁴⁺ sites, and the impact on BrO₃⁻. They found that the difference in bromate formation between ozonation alone and CeO₂ catalytic ozonation decreased as SO₄²⁻ amounts increased from 0 to 5 mM. The diminishing effectiveness of CeO₂ to minimize BrO₃⁻ formation is ascribed to surface Ce⁴⁺ – SO₄²⁻ co-ordination, thus indicating that surface Ce⁴⁺ sites account for most of the BrO₃⁻ minimization during CeO₂ catalytic ozonation.

2.3. Nano-Metal Oxides, SnO₂ and TiO₂

Wu et al. [27] conducted simulation studies to investigate the influence of nano-metal oxides, SnO₂ and TiO₂ on bromate generation in pure water during ozone treatment. Their results showed that ozonation in the presence of nano-metal oxides (SnO₂ and TiO₂) as catalysts, minimized BrO₃⁻ generation to a greater extent, compared to single ozonation. However, nano-TiO₂ was most effective in inhibiting BrO₃⁻ formation. The experimental results showed that the concentrations of residual O₃ and HOBr/OBr⁻ were significantly lesser in nano-TiO₂ catalysed ozonation relative to uncatalysed ozonation and nano-SnO₂ ozonation, indicating that catalytic ozonation with nano-TiO₂ decomposes

more O_3 to HO^\bullet radicals. The lower ozone concentration results in lower $HOBr/OBr^-$, hence minimizing BrO_3^- formation. Furthermore, HO^\bullet radicals can rapidly combine to generate H_2O_2 , which can reduce $HOBr/OBr^-$ to Br^- [28,29]. The presence of humic acid influenced bromate generation. Increasing the humic acid concentration from 0 to 3.0 ppm resulted in a decrease in bromate formation. Humic acid reacts readily with O_3 and hydroxyl radicals, which also reacts with Br^- and $HOBr/OBr^-$ [16,30]. Therefore, a lower concentration of $HOBr/OBr^-$ leads to lesser bromate formation [22].

2.4. Mn Incorporated MCM-41

Xue et al. [31] employed mesoporous Mn incorporated MCM-41 to hinder bromate production during catalytic ozonation of waters containing bromide. A comparison of the three temperature ramping rates (0.5 K min^{-1} , 1 K min^{-1} and 2 K min^{-1}) during calcination of Mn_X -MCM-41 ($X = 40, 80, 100$ and 120 , the molar ratio of Si/Mn), revealed that Mn_{100} -MCM-41 with ramping rate of 1 K min^{-1} showed superior surface characteristics and the greatest bromate inhibition efficiency. A 96.7% inhibition efficiency was achieved after 60 min when compared to ozonation alone. XPS data revealed that Mn_{100} -MCM-41 (1 K min^{-1}) has more oxygen vacancies, which has tendency to adsorb and dissociate H_2O to surface active species [32]. Ozone readily reacts with these surface-active species, resulting in less ozone exposure for Br^- oxidation to $HOBr/OBr^-$, hence minimizing bromate formation. The higher fraction of Mn^{2+} and Mn^{3+} in Mn-MCM-41 enhanced bromate inhibition efficiency.

Xue et al. revealed that the concentration of $HOBr/OBr^-$ during Mn_{100} -MCM-41 ozonation was lower than single ozonation. They explained that Mn_{100} -MCM-41 adsorbs H_2O and dissociates to form surface active species. Ozone then readily reacts with these surface-active species, hence leading to low ozone exposure for Br^- oxidation $HOBr/OBr^-$. Furthermore, hydrogen peroxide was detected in both uncatalysed and Mn_{100} -MCM-41 catalysed ozonation. The concentration of H_2O_2 increased steadily in Mn_{100} -MCM-41 ozonation, but decreased in uncatalysed ozonation, signifying that more reactive oxygen species [32] is formed in the presence of Mn_{100} -MCM-41. These species are capable of consuming $HOBr/OBr^-$ and preventing bromate formation. To verify the role of hydroxyl radicals, TBA (a potential HO^\bullet radical scavenger) was introduced in both single ozonation and Mn_{100} -MCM-41 ozonation. The bromate yield decreased for both processes, thus confirming that HO^\bullet was primarily responsible for BrO_3^- production. In ozonation alone, the decrease in bromate yield is mainly attributed to the decrease in hydroxyl radicals. In Mn_{100} -MCM-41/ O_3 process, the decreased bromate yield is due to the decrease in both hydroxyl radicals and residual ozone. A similar phenomenon was evident with Fe-Cu-MCM-41 [33].

2.5. Fe-MCM-41, Cu-MCM-41 and Fe-Cu-MCM-41

Chen et al. [33] showed that ozonation with Fe-MCM-41, Cu-MCM-41 and Fe-Cu-MCM-41 catalysts considerably reduced BrO_3^- formation. The inhibition activity and bromate yield were as follows: Cu-MCM-41 (28.8 ppb) \approx Fe-MCM-41 (31.5 ppb) $>$ Fe-Cu-MCM-41 (124.5 ppb) $>$ O_3 (432.5 ppb). They attributed the bromate reduction to ozone decomposition by the catalysts, resulting in a reduced amount of ozone for bromate generation [19]. The higher bromate yield in Fe-Cu-MCM-41/ O_3 than in Fe-MCM-41/ O_3 and Cu-MCM-41/ O_3 systems, is due to more HO^\bullet presence in the Fe-Cu-MCM-41/ O_3 system. The presence of both the redox couples, Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu^+ on the catalyst surface (confirmed by XPS analysis) further accelerated ozone decomposition into HO^\bullet radicals. As illustrated in Figure 2, bromate is produced through both the direct and indirect oxidation of Br^- by O_3/HO^\bullet [34].

After the addition of the catalyst, more ozone is consumed, resulting in a hindrance of the direct oxidation of Br^- to $HBrO/BrO^-$ by ozone (a key intermediate reaction for bromate generation), and additional oxidation of $HBrO/BrO^-$ to BrO_3^- [19]. The superior efficiency of Fe-Cu-MCM-41, causes an abundance of hydroxyl radicals. A greater HO^\bullet concentration results in an impediment of pathway 1, thus resulting in a higher bromate build-up [35].

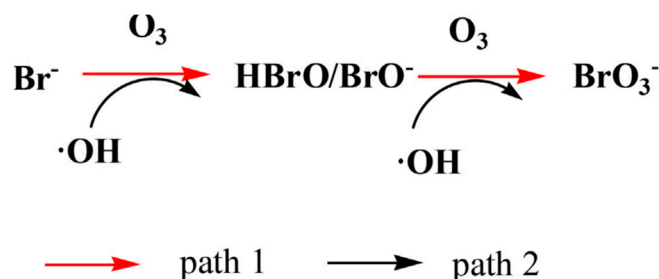


Figure 2. Formation route for bromate.

The addition of t-butanol (TBA) to the Br^- substrate solution, generated less bromate in both single ozonation and ozonation with Fe-Cu-MCM-41. As reported, the bromate formation requires the presence of both ozone and hydroxyl radicals [36]. Bromide is first oxidized by ozone directly to HBrO/BrO^- . Thereafter, the HBrO/BrO^- is oxidized by HO^\bullet to BrO_3^- . Thus, in single ozonation, since the HO^\bullet radicals are scavenged by TBA, bromate formation is primarily due to molecular ozone. In the Fe-Cu-MCM-41/ O_3 process, the ozone concentration in the water significantly decreases due to the surface reactions, and the generated HO^\bullet radicals are also scavenged by TBA. Both actions result in the suppression of the bromate formation pathway, hence, lowering bromate yield.

Bromate production was also inhibited in both ozonation alone and Fe-Cu-MCM-41 catalytic ozonation with the addition of PO_4^{3-} . Bromide yields were found to increase with an increase in PO_4^{3-} dosage. As proposed by Huang, PO_4^{3-} accelerates the generation of H_2O_2 , which reduces HBrO/BrO^- to Br^- , hence constraining BrO_3^- generation [37].

2.6. Fe-Al LDH Supported on Mesoporous Al_2O_3

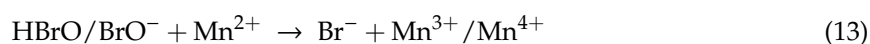
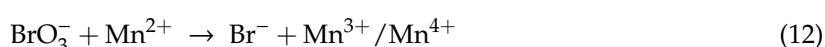
Nie et al. [38] prepared Fe-Al layered double hydroxides (Fe-Al LDH, the molar ratio of $\text{Fe}^{2+}:\text{Fe}^{3+} = 1:10$) supported on mesoporous Al_2O_3 and showed its effectiveness to minimize bromate formation. The BrO_3^- concentration rapidly increased during the uncatalysed ozonation reaching 20 ppb after 60 min of ozone treatment. However, ozonation with Fe-Al LDH/ Al_2O_3 completely inhibited BrO_3^- formation. Furthermore, even when the initial Br^- concentration and ozone dose were increased, the BrO_3^- yield after 60 min of catalytic ozonation stayed below the allowable limit of 10 ppb.

Fe-Al LDH/ Al_2O_3 in the presence of a mixture of phenazone (PZ) and BrO_3^- only, revealed that approximately 45% of BrO_3^- was adsorbed on Fe-Al LDH/ Al_2O_3 and 18% of Br^- was generated. They ascribed the BrO_3^- reduction to Fe^{2+} formed during Fe-Al LDH/ Al_2O_3 preparation, which was confirmed by XPS analysis [39]. However, 82% of BrO_3^- was converted to Br^- during Fe-Al LDH/ Al_2O_3 ozonation of the PZ/ BrO_3^- mixture. The reduction of BrO_3^- to Br^- increased with the ozone dose and BrO_3^- concentration. In contrast, the PZ/ O_3 system could not reduce BrO_3^- to Br^- . Furthermore, when phosphate was added to the Fe-Al LDH/ Al_2O_3 / O_3 system, BrO_3^- reduction was completely suppressed. The presence of phosphate permanently blocked the active surface sites of the catalyst, resulting in the replacement of surface hydroxyl groups and the formation of complexes with Fe^{3+} within the catalyst, thereby decreasing catalytic activity [40,41]. The adsorption of BrO_3^- and the interaction of O_3 with Fe-Al LDH/ Al_2O_3 was suppressed, therefore, poor BrO_3^- reduction is expected. Further investigations indicated that BrO_3^- reduction to Br^- by surface Fe^{2+} is responsible for complete inhibition of BrO_3^- formation. The Fe^{2+} needed for BrO_3^- reduction is generated from surface reactions occurring on Fe-Al LDH/ Al_2O_3 . The Fe^{3+} -intermediate complex on the catalyst surface undergoes electron transfer reactions to produce Fe^{2+} . Furthermore, the reaction of Fe^{3+} with $\text{HO}_2^\bullet/\text{O}_2^\bullet$ forms Fe^{2+} . The results also revealed that bromate reduction was favoured in the presence of different organic pollutants during catalytic ozonation. The amount of surface Fe^{2+} , confirmed by XPS analysis, on Fe-Al LDH/ Al_2O_3 varied for different organic pollutants, suggesting that the structure of the organic pollutant had an impact on the reduction of BrO_3^- .

2.7. Mesoporous Alumina Supported MnOx

Nie et al. [42] investigated the reduction pathway of BrO_3^- generation during ozonation of 2,4-dichlorophenoxyacetic acid (2,4-D) with mesoporous alumina supported MnOx ($\text{MnOx}/\text{Al}_2\text{O}_3$) suspension. The ozonation of 2,4-D in the presence of bromide resulted in a rapid increase in bromate yield. The degradation of 2,4-D was significantly suppressed, while the efficiency of TOC removal decreased significantly from 25.7% to 7%. The catalytic ozonation with $\text{MnOx}/\text{Al}_2\text{O}_3$ significantly inhibited BrO_3^- formation, however, the presence of Br^- did not influence 2,4-D degradation.

In agreement with other studies, HBrO/BrO^- was found to be the main essential intermediate for BrO_3^- formation [18]. During both the uncatalysed and catalysed ozonation, HBrO/BrO^- was rapidly generated. However, BrO_3^- generation was significantly suppressed with $\text{MnOx}/\text{Al}_2\text{O}_3$ in comparison to single ozonation. The trend in the data suggested that different bromine transformation mechanisms existed in the two processes. Bromate reduction occurred over $\text{MnOx}/\text{Al}_2\text{O}_3$ with ozone and 2,4-D, while a rapid increase in Br^- yield was observed. The results confirmed that BrO_3^- was reduced to Br^- on the surface of $\text{MnOx}/\text{Al}_2\text{O}_3$ during ozonation. Electron transfer reactions occurred during the O_3 adsorption and decomposition processes on the surface of the catalyst [43–45]. The UV–Vis absorption spectrum of MnOx showed the existence of Mn in different oxidation states, namely Mn^{2+} , Mn^{3+} and Mn^{4+} [46]. Therefore, Mn^{2+} is responsible for promoting O_3 to eliminate organic pollutants and also assist in inhibiting BrO_3^- formation. The proposed reactions on $\text{MnOx}/\text{Al}_2\text{O}_3$ in the presence of ozone occurs as follows [42]:



Reaction (14) proposes the generation of H_2O_2 in both uncatalysed and catalytic ozonation. The results showed that H_2O_2 concentration was remarkably lower in uncatalysed ozonation than in $\text{MnOx}/\text{Al}_2\text{O}_3$ catalytic ozonation. This trend suggests that in catalytic ozonation, reaction (14) is suppressed, since more HO_2^{\bullet} is used up by reactions (10) and (11), hence leading to increased generation of Mn^{2+} . This confirmed that the presence of different oxidation states of manganese is responsible for controlling BrO_3^- generation.

2.8. $\text{Ce}_x\text{Zr}_{x-1}\text{O}_2$ Mixed Oxides

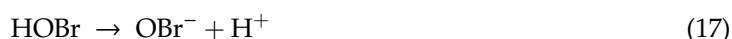
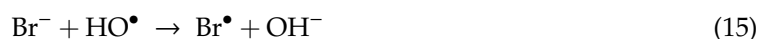
Yang et al. [47] prepared mixed oxides $\text{Ce}_x\text{Zr}_{x-1}\text{O}_2$ ($x = 0.16, 0.50, 0.75, 0.9$) and CeO_2 to study BrO_3^- reduction during ozonation of Br^- containing filtered water. The results indicated that catalytic ozonation with $\text{Ce}_x\text{Zr}_{x-1}\text{O}_2$ and CeO_2 minimized bromate formation better than ozonation alone. They concluded that the $\text{Ce}_x\text{Zr}_{x-1}\text{O}_2$ mixed oxides and CeO_2 effectively suppressed the oxidation of Br^- by O_3 and HO^{\bullet} radicals. Furthermore, the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ mixed oxide displayed the best catalytic activity for BrO_3^- minimization, with 53% of BrO_3^- formation being reduced after 20 min of ozonation. The adsorption of Br^- and BrO_3^- on catalyst surface were not detected, since anions have no affinity for the neutral or negatively charged oxide surface. Furthermore, the catalyst material exhibited good stability, since no leaching of metal ions were detected during the ozonation process.

To confirm the role of O_3 and HO^{\bullet} radicals in BrO_3^- inhibition, p-chlorobenzoic acid (pCBA), a HO^{\bullet} scavenger was introduced to monitor HO^{\bullet} radicals. HPLC analysis revealed that pCBA concentration decreased rapidly with ozone treatment time, and its concentration was considerably lower in $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ ozonation than in single ozonation. This indicates that $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ mixed oxide significantly promoted the decomposition of O_3 to HO^{\bullet} radicals during the catalytic ozonation

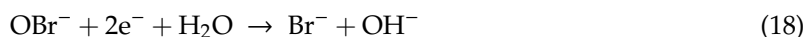
process. Their results also showed that BrO_3^- formation and O_3 decomposition was extremely rapid during the first 5 min of ozonation, further confirming that HO^\bullet radicals play a major role during BrO_3^- formation. The organic compounds in water favours organic/ HO^\bullet reactions more than $\text{Br}^-/\text{HO}^\bullet$ reactions, since the rate of reaction for oxidative degradation of organic compounds by HO^\bullet radicals is faster than that for oxidizing Br^- by HO^\bullet radicals [48]. Since the HO^\bullet radicals facilitate the efficient degradation of organic substituents, therefore, the suppression of the oxidation of Br^- is favoured, leading to the minimization of BrO_3^- yield.

2.9. TiO_2

Parrino et al. [49] investigated simultaneous ozonation and photocatalysis for purifying wastewater containing formic acid/4-nitrophenol and bromide ions. The initial ozonation experiments performed on formate and bromide ions in the presence and absence of TiO_2 , showed similar degradation rates, suggesting that reactions occurring on the TiO_2 surface did not contribute to the degradation of the target compounds [50]. It was also observed that the oxidation of formate was not affected by the presence of bromide ion and the oxidation of bromide to bromate occurred only after the consumption of formate ions. Bromide ions reacted with hydroxyl radicals generated during photocatalysis, according to the following reaction scheme:



Lastly, the photoelectrons generated on the photocatalyst surface reduced the hypobromite species to bromide.



As illustrated, these pathways eventually lead to the recovery of bromide ion, Equation (18). Furthermore, if solution pH is in the range 6–8, a secondary pathway facilitates the conversion of hypobromous acid to bromide. The generated HOBr, as shown in Equation (16), primarily exists in its protonated form, and H_2O_2 generated during the photocatalytic reaction, acts as a scavenger for hypobromite, by reducing it to bromide [51].

From this outcome, they concluded that bromate generation can be prevented by interrupting the ozone treatment as soon as the oxidation of the organic species is almost complete. Furthermore, reducing bromate is also a more practical way to minimize its accumulation, and as per the previous reports, photocatalysis alone is efficient to convert bromate to bromide [51]. When 4-nitrophenol was substituted in the place of the formate ion, the formation of bromate, took place once again only after the disappearance of 4-nitrophenol, and was found to be faster than with formate ion. This implies that the type of organic contaminant in the water plays a decisive role in the amount of bromate formed.

2.10. $\beta\text{-FeOOH}/\text{Al}_2\text{O}_3$

Nie et al. [52] investigated bromate formation during the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) in Br^- containing water under uncatalysed and $\beta\text{-FeOOH}/\text{Al}_2\text{O}_3$ catalysed ozonation conditions. In uncatalysed ozonation, bromate yield increased rapidly to a maximum value of 21.5 ppb, but in $\beta\text{-FeOOH}/\text{Al}_2\text{O}_3$ ozonation, BrO_3^- formation was completely inhibited.

Furthermore, the experimental data showed that about 68% of BrO_3^- was adsorbed on the surface of $\beta\text{-FeOOH}/\text{Al}_2\text{O}_3$ during 2,4-D degradation, and with the addition of ozone, BrO_3^- was completely converted into Br^- within 180 min. In ozonation without 2,4-D, BrO_3^- was not reduced to Br^- . However, BrO_3^- reduction was found to only occur with selected organic contaminants.

Results also showed that no Fe^{2+} was formed when $\beta\text{-FeOOH}/\text{Al}_2\text{O}_3$ was present in water alone, however, a small amount of surface Fe^{2+} was observed when $\beta\text{-FeOOH}/\text{Al}_2\text{O}_3$ in water was ozonated.

A further increase in surface Fe^{2+} was noticed when water in the presence of $\beta\text{-FeOOH}/\text{Al}_2\text{O}_3$ and 2,4-D was ozonated. The quantity of surface Fe^{2+} decreased rapidly when BrO_3^- was introduced, signifying that Fe^{2+} was responsible for BrO_3^- conversion to Br^- [39,53]. The Fe^{2+} generated on $\beta\text{-FeOOH}/\text{Al}_2\text{O}_3$ arises from the reaction of Fe^{3+} with $\text{HO}_2^{\bullet-}/\text{O}_2^{\bullet-}$, and the complexation of surface Fe^{3+} with the oxy-functional groups (-OH, -COOH). The organic pollutants or their oxygenated intermediates improves the reaction of Fe^{3+} with $\text{HO}_2^{\bullet-}/\text{O}_2^{\bullet-}$, hence resulting in more surface Fe^{2+} , which causes a higher BrO_3^- reduction rate.

2.11. Fe-Cu-MCM-41

Chen et al. [29] investigated the formation of bromate in the presence of Fe-Cu-MCM-41 during ozonation of Br^- /Diclofenac containing water. They found that Fe-Cu-MCM-41 decreased the concentration of dissolved ozone, hence diminishing the direct reaction of O_3 with Br^- . Ozonation of water containing only bromide ions, produced 276 ppb bromate, but in the presence of Fe-Cu-MCM-41 the bromate yield decreased to 151 ppb. Bromide in the presence of Diclofenac (DCF), saw a significant drop in bromate formation for both O_3 alone and Fe-Cu-MCM-41/ O_3 . During the initial treatment process, Br^- is oxidized to HBrO/BrO^- and then to BrO_3^- under the action of O_3 and HO^{\bullet} radicals. The presence of DCF and its intermediates influences BrO_3^- formation by competing with Br^- and HBrO/BrO^- for O_3 and HO^{\bullet} radicals, thus inhibiting bromate formation. Also, the degradation of DCF decreases the solution pH to acidic, and bromate formation is not favoured in acidic medium [35].

2.12. Perovskite-Type Oxides, LaFeO_3 and LaCoO_3

Y. Zhang et al. [54] synthesized two perovskite-type oxides, LaFeO_3 and LaCoO_3 , and examined their capacity to degrade benzotriazole (BZA) and minimize BrO_3^- formation in water during ozonation. The ozonation of an aqueous mixture of BZA and Br^- generated the most amount of BrO_3^- . The bromate yield increased sharply for the first 20 min of ozonation and then showed a decreasing trend up to 120 min. The bromate yield decreased significantly after the addition of catalyst, especially during the first 30 min of ozonation, but the conversion of Br^- was faster with LaCoO_3 compared with LaFeO_3 . The concentration of HBrO/BrO^- was found to be higher in LaCoO_3 ozonation than with LaFeO_3 , which explains its superior BrO_3^- minimization ability. The production of $\text{HO}_2^{\bullet-}/\text{O}_2^{\bullet-}$ resulted in the generation of H_2O_2 , which also contributed to the reduction of BrO_3^- to HBrO/BrO^- .

Y. Zhang et al. [54] further illustrated the reaction mechanism of LaFeO_3 and LaCoO_3 facilitated ozonation of benzotriazole (BZA) and BrO_3^- minimization. They concluded that LaFeO_3 did not catalytically promote molecular ozone decomposition to reactive oxygen species (ROS), which is needed for BZA degradation, but instead rapidly reduced BrO_3^- . The reaction of H_2O_2 over LaFeO_3 , suggested that H_2O_2 was used up in the presence of LaFeO_3 and the consumed H_2O_2 was not used to produce HO^{\bullet} radicals. The H_2O_2 in $[\text{Fe-H}_2\text{O}_2]_S$ more easily reduces BrO_3^- to HOBr/OBr^- .

On the other hand, LaCoO_3 promoted the decomposition of ozone to ROS, which facilitated faster degradation of BZA and oxidation of Br^- to BrO_3^- . Therefore, HOBr/OBr^- concentration was lower in the presence of LaCoO_3 than in ozonation alone. LaCoO_3 accelerated the decomposition of BZA to H_2O_2 . The H_2O_2 reduced BrO_3^- directly to form more HOBr/OBr^- . The cyclic reaction of $\text{Co}^{3+}/\text{Co}^{2+}$ also promoted BZA degradation and inhibition of BrO_3^- reduction.

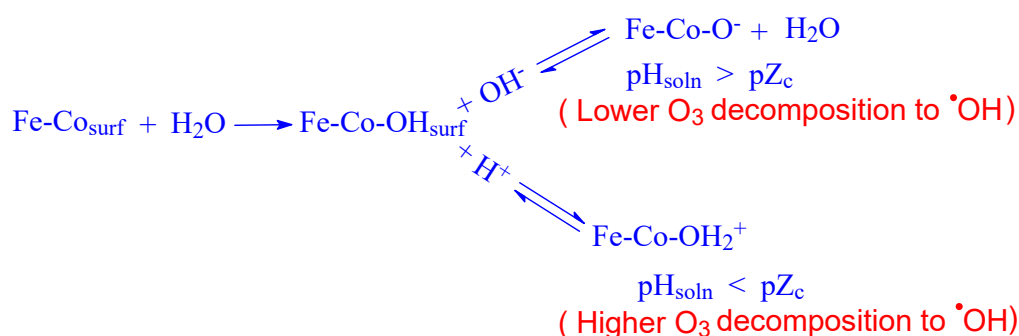
2.13. HZSM-5 Zeolites

T. Zhang et al. [55] studied the influence of H^+ -form high silica ZSM-5 (HZSM-5) zeolites with different Si/Al molar ratios (i.e., 25–300) on bromate formation. Their results showed that bromate yield increased with time in a single ozonation, $\text{O}_3/\text{HZSM-5}$ and O_3/CeO_2 . The bromate concentration in $\text{O}_3/\text{HZSM-5}$ was significantly lower than in single ozonation and in O_3/CeO_2 . The HZSM-5 with Si/Al ratios of 300 and 25 showed superior capacity for bromate minimization and reduced approximately 58% bromate formation potential after 20 min of ozone treatment, while CeO_2 only reduced 22%.

Further studies on HZSM-5 (Si/Al = 300) showed that its high efficiency for bromate minimization is related to its affinity to adsorb OBr^- , a major intermediate in bromate formation [1]. The results have shown that HZSM-5 had no affinity to adsorb Br^- , BrO_3^- and HOBr , therefore no direct electron transfer reaction is expected on HZSM-5. However, the majority of OBr^- was rapidly adsorbed onto HZSM-5 within 0.5 min. They then concluded that the specific adsorption of OBr^- on the HZSM-5 prevents the oxidation of OBr^- to BrO_3^- in water. Their results also detected the presence of H_2O_2 in both single ozonation and ozonation with HZSM-5. Considerably higher yields of H_2O_2 were detected in single ozonation than in $\text{O}_3/\text{HZSM-5}$ process, and the HZSM-5 neither adsorbed nor decomposed H_2O_2 in water. The lower H_2O_2 concentration in $\text{O}_3/\text{HZSM-5}$ leads to lower bromate yields.

2.14. $\text{FeO}_x/\text{CoO}_x$

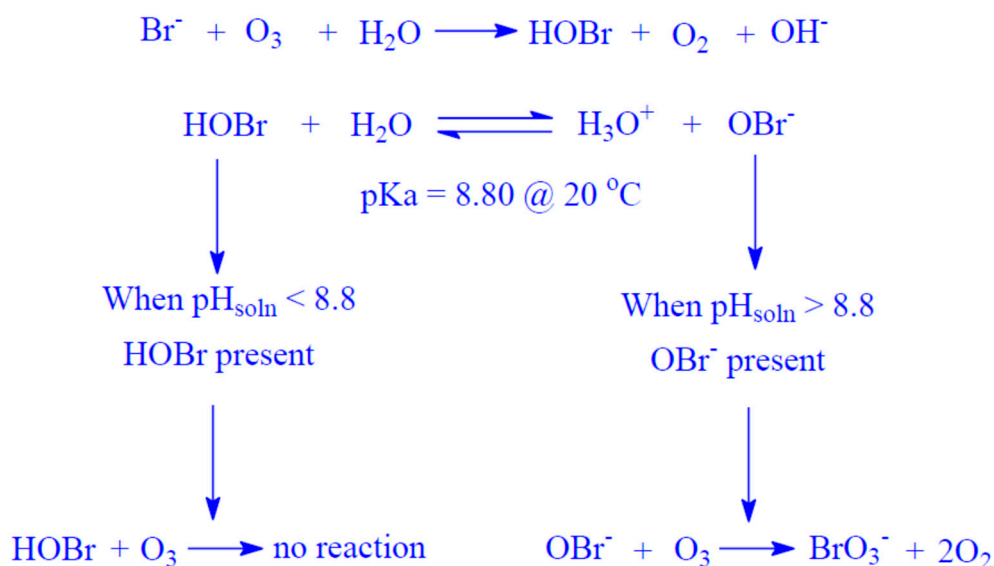
Gounden et al. [56], conducted a study on the degradation of hazardous halohydrin, 2,3-dibromopropan-1-ol (2,3-DBP) in water by ozonation alone and ozonation with Co loaded on Fe prepared by co-precipitation (Co-ppt) and a simple physical mixing method (Mixed). Their results showed that debromination of 2,3-DBP produced large quantities of Br^- and BrO_3^- ions. The Fe:Co (Mixed) catalyst was found to be more effective in suppressing the generation of bromate than the Fe:Co (Co-ppt) catalyst. The presence of Fe:Co (Mixed) lowered the solution pH from 6.8 to 5.7, which was an ideal condition for inhibiting bromate formation. The reaction pathway for conversion of Br^- to BrO_3^- was described in the presence of Fe-Co (Mixed) catalyst. Firstly, since pH of the initial solution (5.7), is higher than the pZc value (5.1) of the Fe-Co (Mixed) catalyst, its surface can comprise mostly of negative Fe-Co⁻ active sites (Scheme 1). These sites repel the negatively charged bromide ions, thus preventing electron transfer reactions on the catalyst surface, resulting in a lower bromate yield.



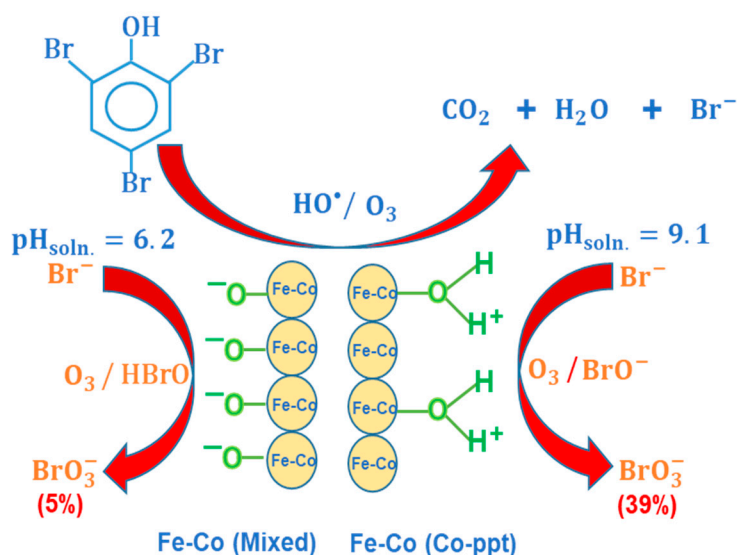
Scheme 1. Reaction pathway for formation of protonated/deprotonated Fe-Co surface in water.

Secondly, since the pH of the initial solution is much lower than the pKa (8.8) of the HOBr/OBr^- system, an equilibrium shift occurs to the left, thus favoring a higher yield of HOBr and lower OBr^- . As ozone is more reactive towards HOBr than OBr^- , a decrease in bromate yield is anticipated (Scheme 2).

A similar pattern of bromate formation, as illustrated in Scheme 3, was observed when 2,4,6-Tribromophenol (2,4,6-TBP) was ozonated with Fe-Co metal oxides. Using Fe-Co (Mixed) catalyst, only 5% of the available bromide was oxidized to bromate, whereas with Fe-Co (Co-ppt), 39% of bromide was converted.



Scheme 2. Pathway for inhibition/formation of bromate in catalytic ozonation.

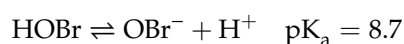


Scheme 3. Reaction pathways for bromate formation during Fe-Co catalysed ozonation and degradation of 2,4,6-TBP in water.

3. Factors Affecting Bromate Minimization

3.1. Effect of Initial Solution pH

Previous studies have shown that lowering of pH to below 7, preceding ozonation results in a decrease in bromate formation [57]. A decrease of one pH-unit results in 50–63% reduction in BrO_3^- formation [58]. This decrease has been attributed to two factors: (i) At $\text{pH} < 7$, oxidized bromide is likely to primarily be found as hypobromous acid (HOBr), resulting in limited amounts of hypobromite (OBr^-) available for reaction with ozone [18,59]:



As the solution pH is increased, the concentration of OBr^- increases, hence promoting BrO_3^- production, since OBr^- is more reactive with ozone than HOBr [1]. The main oxidant for bromate formation in natural water is the hydroxyl radical. At a lower pH, the conversion of molecular ozone to hydroxyl radicals is low, therefore, the amount of bromate formed through the hydroxyl

radical pathway is limited. At lower pH, the ratio of hydroxyl radical to ozone tends to be lower than at higher pH. The lowering of pH can also be problematic because it can result in poor or incomplete degradation of organic substrates, which can lead to the formation of various hazardous brominated organic compounds. Furthermore, for high alkalinity wastewaters, the lowering of pH is not economically feasible.

Li et al. [19] studies confirmed that bromate formation increased significantly in ozonation alone as pH was increased from 6.3 to 9.5. This can be due to fact that in alkaline medium (i) OH^- shifts the acid/base equilibria of HOBr ($\text{pK}_a = 8.8$) towards OBr^- , which reacts readily with both O_3 and HO^\bullet [1], and (ii) OH^- decomposes O_3 to HO^\bullet radicals, which enhances BrO_3^- formation. Their Ce_{66} -MCM-48/ O_3 system minimized BrO_3^- formation and was also pH dependant. For pH range of 7.6–8.6, a higher minimization efficiency of 87–91% was attained by Ce_{66} -MCM-48 after 10 min of ozonation. With a decrease in pH to 6.3, the inhibition efficiency decreased to 76%. When the pH was increased to 9.5, the minimization efficiency of Ce_{66} -MCM-48 reduced to 82%. At high pH, OBr^- is the major species. It reacts rapidly with both O_3 and HO^\bullet to form significant amounts of BrO_3^- .

The experiments conducted by T. Zhang et al. [22] at controlled pH revealed that BrO_3^- yield increased rapidly in both single ozonation and in the O_3/CeO_2 system as the pH was increased from 5.5 to 8.9. An 84% reduction in BrO_3^- yield was achieved at pH 6.2. They attributed the catalytic activity and BrO_3^- reduction to the surface charge of CeO_2 and intermediary HOBr/OBr^- speciation, which are pH dependent. When the pH of the solution is close to the pH_{pzc} of CeO_2 (6.6), its surface is not charged. If solution pH is below the pH_{pzc} of CeO_2 its surface becomes positively charged, due to protonation of its surface hydroxyl sites by water. This condition increases the proportion of HOBr , hence minimizing BrO_3^- formation. If solution pH is above the pH_{pzc} of CeO_2 its surface becomes negatively charged due to deprotonation of surface hydroxyl sites, thus continuously increasing the quantity of OBr^- , which favours the formation of bromate ion.

Wu et al. [27] monitored BrO_3^- formation at different pH values during single ozonation and ozonation with nano-TiO₂. Their results indicated that ozonation with nano-TiO₂ favoured the formation of BrO_3^- as solution pH increased initially from 6.0 to 7.9. They also concluded that at high pH, rapid ozone decomposition is favoured, hence increasing production of hydroxyl radicals, resulting in higher BrO_3^- formation. A higher proportion of OBr^- is present at pH 7.9, which would also promote BrO_3^- formation. The increasing pH led to a slight decrease in BrO_3^- formation rate from 73.75% to 71.32%, displaying a reduced activity for nano-TiO₂.

Xue et al. [31] observed that the initial solution pH had a significant influence on bromate formation during ozonation in the presence of Mn_{100} -MCM-41 (1 K min^{-1}). The inhibition efficiencies for bromate formation were 96.7%, 83.4% and 68.2% at pH 6.5, 7.5 and 9.5 respectively. The increase in bromate formation with pH, is influenced by the equilibrium of HOBr/OBr^- and the stability of ozone in aqueous media. The increasing pH favours the formation of more OBr^- ions, which readily decomposes O_3 to form HO^\bullet radicals, therefore, accelerating bromate formation. In acidic conditions, ozone is stable and more HOBr is present, therefore, bromate formation is suppressed [60].

Chen et al. [33] observed that by increasing the initial solution pH from 3.0 to 9.0 increased bromate formation for both uncatalysed and Fe-Cu-MCM-41 catalysed ozonation, however, for the entire pH range Fe-Cu-MCM-41/ O_3 process generated lower bromate yield. As the pH increased to 9.0, bromate steadily accumulated, reaching 913 ppb in single ozonation and 335 ppb in Fe-Cu-MCM-41 ozonation. At the acidic condition, HBrO is favoured ($\text{pH} < \text{pK}_a$), and since O_3 is more stable, fewer HO^\bullet radicals are formed. As HBrO predominantly reacts with HO^\bullet , the oxidation pathway 2 in Figure 2 is suppressed and a reduced amount of bromate is formed. Under basic conditions, the equilibrium shifts towards BrO^- , which is highly reactive towards both O_3 and HO^\bullet , resulting in accelerated bromate production [35].

Zhang et al. studied the influence of pH on bromate formation for the $\text{O}_3/\text{HZSM-5}$ system [55]. In ozonation alone, it was observed that as solution pH increased from 6.6 to 9.3, the bromate yield increased rapidly from 4.9 ppb to 27 ppb. In catalytic ozonation with HZSM-5, the bromate yield

increased more steadily from 2.8 ppb to 9.4 ppb. They attributed the drop in bromate formation to the adsorption of BrO^- on HZSM-5 at different pH levels. Considering the equilibrium constant of 10^{-9} for HOBr/OBr^- , the fraction of BrO^- in HOBr/OBr^- at pH 8.0 and pH 9.3 is approximately 14% and 76%, respectively. This would mean that higher amounts of BrO^- can be adsorbed on HZSM-5 at pH 9.3 than at pH 8.0, so would the bromate reduction efficiency. However, their results have shown that the percent reduction in bromate formation increased only by 7.6%, when the solution pH was raised from 8.0 to 9.3. Since BrO^- is more reactive towards ozone than HOBr , and the $\text{HO}^\bullet/\text{OBr}^-$ reaction rate is approximately two times that of $\text{HO}^\bullet/\text{HOBr}$ [1]. Therefore, the increase in pH leads to a substantial increase in bromate yield in single ozonation. In HZSM-5 ozonation, O_3 and HO^\bullet compete with HZSM-5 for BrO^- , thus resulting in lower bromate formation at higher pH.

Kishimoto and Nakamura [61] concluded from their studies that hydroxyl radicals are more crucial than molecular ozone in bromate production. They demonstrated that in ozonation alone, BrO_3^- yield increased as Br^- concentration decreased at neutral pH in the absence of 4-chlorobenzoic acid (4-CBA). However, BrO_3^- yields considerably decreased compared to Br^- removal at acidic pH and in the presence of 4-CBA. Although acidic pH decreased BrO_3^- generation, it limited the oxidation capacity of ozone for successful 4-chlorobenzoic acid degradation. Therefore, the acidification during ozonation is favorable for BrO_3^- minimization, but it has the disadvantage of affecting the removal efficiency of organic pollutants from water.

3.2. Effect of Initial Bromide Concentration

Several studies have shown that the presence of small quantities of bromide ion can result in the generation of significant amounts of bromate ion during single ozonation. Bromate ion yield increased as bromide ion concentration increased. A few studies were conducted to investigate the influence of initial bromide concentration on the bromate formation during catalytic ozonation.

Wu et al. [27] examined BrO_3^- formation for various initial Br^- concentrations during single ozonation and ozonation with nano-TiO₂. The data indicated that in single ozonation BrO_3^- yield increased rapidly as a function of initial Br^- concentration, however in ozonation with nano-TiO₂ the BrO_3^- yield was significantly lower. When initial Br^- concentration increased from 0.4 ppm to 1.2 ppm, the reduction rate of BrO_3^- decreased from 67.22% to 47.11%, suggesting that the activity of nano-TiO₂ is severely inhibited with an increase in initial Br^- concentration.

The experiments conducted by T Zhang et al. [22] to study the influence of initial bromide concentration on bromate production showed that in single ozonation BrO_3^- yield increased rapidly from 0.5 ppm to 2 ppm, as the concentration of bromide ion increased. In CeO₂ catalysed ozonation, BrO_3^- formation was significantly suppressed for Br^- concentrations ≤ 1.0 ppm, however, for Br^- concentrations > 1.0 ppm, BrO_3^- yield started to increase rapidly. The BrO_3^- yield in CeO₂ catalysed ozonation was always lower than that obtained with uncatalysed ozonation.

3.3. Effect of Ozone Dosage

Sufficient availability of ozone showed an increase in the bromate ion formation, until all bromide ion was converted to bromate ion [58]. von Gunten and Hoigne [18] have introduced a standard measure for the ozone concentration (C) as a function of reaction time (t), which is defined as the Ct value (mg/L·min) for ozone exposure. An increase in the quantity of ozone improves the Ct value during ozone treatment of water. Wu et al. [27] demonstrated that BrO_3^- yield kept on increasing as ozone concentration was increased in both single ozonation and nano-TiO₂ ozonation, that is, for all experiments BrO_3^- formation increased linearly as the 'Ct value increased. When ozone dosage was increased from 2.22 ppm to 4.62 ppm, an improvement in the BrO_3^- reduction rate from 62.94% to 75.66% was observed. The BrO_3^- formation rates in single ozonation were found to be much higher than in catalytic ozonation, however, no explanation was given for this trend.

Zhang et al. [55] showed that bromate yield increased rapidly from 7.8 ppb to 95 ppb in single ozonation as the ozone concentration was increased from 0.38 ppm to 1.16 ppm. In catalytic ozonation

with HZSM-5, bromate yield increased much slower (from 4.3 ppb to 21 ppb) for the same increase in ozone dose. HZSM-5 may have depleted the concentrations of ozone and/or intermediate species, which are needed for bromate formation.

3.4. Influence of Temperature Changes

The increasing temperature generally increases bromate ion production in water during ozonation. The effects of temperature are due to the following facts: (i) Ozone decomposition into HO^\bullet radicals is favoured at higher temperatures; (ii) an increase in temperature enhances the reaction rate and (iii) the pK_a of the HOBr/OBr^- system is temperature dependent.

The experimental data showing the influence of solution temperature on bromate minimization efficiency indicated that in the temperature range of 15°C to 30°C Ce_{66} -MCM-48 catalytic ozonation showed nearly the same minimization efficiency as that of single ozonation [19]. This temperature-independent feature of Ce_{66} -MCM-48 is advantageous for water treatment by ozonation.

The influence of solution temperature on BrO_3^- formation showed that, in single ozonation, the BrO_3^- yield increased moderately when the temperature was increased from 5 °C to 15 °C, and increased more sharply when raised from 15 °C to 25 °C. The generation of BrO_3^- in CeO_2 ozonation was found to be similar to single ozonation, however much less BrO_3^- was produced in CeO_2 ozonation [22].

3.5. Influence of Catalyst Dosage

Generally, the bromate yield increases as a function of catalyst dose. For example, bromate production with increasing nano- TiO_2 dosage (0 to 200 ppm) investigated by Wu et al. [27] showed that when nano- TiO_2 dose was increased from 0 to 100 ppm, the BrO_3^- reduction rate increased from 0% to 72.59%. However, when nano- TiO_2 dose increased from 100 to 200 ppm, the BrO_3^- reduction rate only went up to 74.27%. The nanoparticles have extremely high surface area, therefore, increasing nano- TiO_2 dosage would result in more active catalytic sites for surface reactions. However, in aqueous solution, ozone concentrations are limited, hence the marginal increase in BrO_3^- reduction rate.

4. Conclusions and Recommendations

The literature indicates that catalytic ozonation using appropriate catalyst materials is a better solution for bromate minimization than uncatalysed ozonation. However, there is still a need for more efficient and practically applicable catalysts to be explored for complete elimination of bromate formation during ozonation. All catalysts reported were able to significantly minimize BrO_3^- formation in comparison to ozonation alone, however, only few were able to minimize bromate formation below the 5 ppb limit. The following bromate inhibition strategies/mechanisms during catalytic ozonation of bromide containing waters were proposed:

- Increasing the number of hydroxyl groups on the catalyst surface resulted in enhanced ozone decomposition to HO^\bullet radicals, thus limiting the contribution of direct O_3 for the sequential oxidation of $\text{Br}^- \rightarrow \text{HOBr}/\text{OBr}^- \rightarrow \text{BrO}_3^-$. The formation of excess HO^\bullet is beneficial for removal of organic pollutants from the water.
- Redox reactions on the catalyst surface causes inhibition of $\text{Br}^- \rightarrow \text{HOBr}/\text{OBr}^-$ and in some cases reduction of BrO^\bullet to HOBr/OBr^- , thus limiting bromate formation. The lesser HOBr/OBr^- concentration leads to lesser BrO_3^- .
- The generation of hydrogen peroxide was detected in most catalytic ozonation systems, but was found to be lower than in ozonation alone. The lesser H_2O_2 means lesser HO^\bullet radicals, therefore, the oxidation rate of HOBr/OBr^- to BrO^\bullet to BrO_3^- is diminished. Contrary to this, some authors observed an increase in H_2O_2 , which they attributed to the reactive oxygen species, which are capable of consuming HOBr/OBr^- . Further work on the relationship between H_2O_2 generation and bromate inhibition is therefore needed.

- The presence of phosphate and humic acid had a tendency to limit bromate formation, however, high levels of phosphate and humic acid can result in poor water quality.
- The limited studies on photocatalytic ozonation of bromide containing waters showed that the concentration of hypobromite species can be minimized by the photoelectrons generated on the photocatalyst surface, thus contributing to bromate reduction.
- Bromate reduction was enhanced in the presence of certain organic compounds, due to electron transfer reactions on the catalyst surface.
- Some catalysts have an affinity to adsorb critical intermediate species (OBr^-) needed for bromate formation.
- Mixed metal oxides were found to effectively minimize bromate formation by simply lowering the initial solution pH to more acidic levels.

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References and Note

1. von Gunten, U. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Res.* **2003**, *37*, 1469–1487. [[CrossRef](#)]
2. Heeb, M.B.; Criquet, J.; Zimmermann-Steffens, S.G.; von Gunten, U. Oxidative treatment of bromide-containing waters: Formation of bromine and its reactions with inorganic and organic compounds—A critical review. *Water Res.* **2014**, *48*, 15–42. [[CrossRef](#)] [[PubMed](#)]
3. Neal, C.; Neal, M.; Hughes, S.; Wickham, H.; Hill, L.; Harman, S. Bromine and bromide in rainfall, cloud, stream and groundwater in the Plynlimon area of mid-Wales. *Hydrol. Earth Syst. Sci.* **2007**, *11*, 301–312. [[CrossRef](#)]
4. Flury, M.; Papritz, A. Bromide in the natural environment: Occurrence and toxicity. *J. Environ. Qual.* **1993**, *22*, 747–758. [[CrossRef](#)]
5. Yuita, K. Iodine, bromine and chlorine contents in soils and plants of Japan. *Soil Sci. Plant Nutr.* **1983**, *29*, 403–428. [[CrossRef](#)]
6. Kittel, H. Substances Usable in Substitution of 2-nitropropane and 1,2 Dibromoethane (Ersatzstoffe für 2-nitropropan und 1,2 dibromoethan). Schriftenreihe Gefährliche Arbeitsstoffe, 1983, (No. 11. Dortmund. Wirtschaftsverlag NW, Bremerhaven.).
7. Bowen, H.J.M. *Environmental Chemistry of the Elements*; Academic Press: London, UK, 1979.
8. Krasner, S.W.; McGuire, M.J.; Jacangelo, J.G.; Patania, N.L.; Reagan, K.M.; Aieta, E.M. Occurrence of DBP's in US drinking water. *J. Am. Water Works Assoc.* **1989**, *81*, 41–53. [[CrossRef](#)]
9. *Survey on Bromide in Drinking Water and Impacts on DBP Formation*; American Water Works Research Foundation: Denver, CO, USA, 1994.
10. Legube, B.; Parinet, B.; Berne, F.; Croue, J.-P. Bromate Surveys in French Drinking Waterworks. *Ozone-Sci. Eng.* **2002**, *24*, 293–304. [[CrossRef](#)]
11. Kruihof, J.C.; Kamp, P.C.; Martijn, B.J. UV/H₂O₂ Treatment: A Practical Solution for Organic Contaminant Control and Primary Disinfection. *Ozone-Sci. Eng.* **2007**, *29*, 273–280. [[CrossRef](#)]
12. Kurokawa, Y.; Maekawa, A.; Takahashi, M.; Hayashi, Y. Toxicity and carcinogenicity of potassium bromate—a new renal carcinogen. *Environ. Health Persp.* **1990**, *87*, 309–335.
13. National Primary Drinking Water Regulations. *Stage 2 Disinfectants and Disinfection By-Products Rule*; US Environmental Protection Agency: Washington, DC, USA, 2006; Volume 71, pp. 387–493.
14. Song, R.; Amy, G.L.; Westerhoff, P.; Minear, R. Bromate minimization during ozonation. *J. Am. Water Works Assoc.* **1997**, *89*, 69–78. [[CrossRef](#)]

15. Richardson, L.; Burton, D.T.; Helz, G.R. Residual Oxidant Decay and Bromate Formation in Chlorinated and Ozonated Sea-Water. *Water Res.* **1981**, *15*, 1067. [[CrossRef](#)]
16. Molnar, J.J.; Agbaba, J.R.; Dalmacija, B.D.; Klasnja, M.T.; Dalmacija, M.B.; Kragulj, M.M. A Comparative Study of the Effects of Ozonation and TiO₂-catalyzed Ozonation on the Selected Chlorine Disinfection By-product Precursor Content and Structure. *Sci. Total Environ.* **2012**, *425*, 169–175. [[CrossRef](#)] [[PubMed](#)]
17. von Gunten, U.; Bruchet, A.; Costentin, E. Bromate formation in advanced oxidation processes. *J. Am. Water Works Assoc.* **1996**, *88*, 53–65. [[CrossRef](#)]
18. von Gunten, U.; Hoigne, J. Bromate Formation during Ozonation of Bromide-Containing Waters: Interaction of Ozone and Hydroxyl Radical Reactions. *Environ. Sci. Technol.* **1994**, *28*, 1234–1242. [[CrossRef](#)] [[PubMed](#)]
19. Li, W.; Lu, X.; Xu, K.; Qu, J.; Qiang, Z. Cerium incorporated MCM-48 (Ce-MCM-48) as a catalyst to inhibit bromate formation during ozonation of bromide-containing water: Efficacy and mechanism. *Water Res.* **2015**, *86*, 2–8. [[CrossRef](#)] [[PubMed](#)]
20. Pelle, K.; Wittmann, M.; Lovrics, K.; Noszticzius, Z. Mechanistic Investigations on the Belousov–Zhabotinsky Reaction with Oxalic Acid Substrate. 2. Measuring and Modeling the Oxalic Acid–Bromine Chain Reaction and Simulating the Complete Oscillatory System. *J. Phys. Chem. A* **2004**, *108*, 7554–7562. [[CrossRef](#)]
21. Heckert, E.G.; Seal, S.; Self, W.T. Fenton-Like Reaction Catalyzed by the Rare Earth Inner Transition Metal Cerium. *Environ. Sci. Technol.* **2008**, *42*, 5014–5019. [[CrossRef](#)]
22. Zhang, T.; Chen, W.; Ma, J.; Qiang, Z. Minimizing bromate formation with cerium dioxide during ozonation of bromide-containing water. *Water Res.* **2008**, *42*, 3651–3658. [[CrossRef](#)]
23. Hiroki, A.; LaVerne, J.A. Decomposition of hydrogen peroxide at water-ceramic oxide interfaces. *J. Phys. Chem. B* **2005**, *109*, 3364–3370. [[CrossRef](#)]
24. Acero, J.L.; Haderlein, S.H.; Schmidt, T.; Suter, M.J.F.; von Gunten, U. MTBE oxidation by conventional ozonation and the combination ozone/hydrogen peroxide: Efficiency of the processes and bromate formation. *Environ. Sci. Technol.* **2001**, *35*, 4252–4259. [[CrossRef](#)]
25. Aubry, J.M. Search for singlet oxygen in the decomposition of hydrogen peroxide by mineral compounds in aqueous solutions. *J. Am. Chem. Soc.* **1985**, *107*, 5844–5849. [[CrossRef](#)]
26. Peak, D.; Ford, R.G.; Sparks, D.L. An in situ ATR-FTIR investigation of sulfate bonding mechanisms on goethite. *J. Colloid Interface Sci.* **1999**, *218*, 289–299. [[CrossRef](#)] [[PubMed](#)]
27. Wu, Y.; Wu, C.; Wang, Y.; Hu, C. Inhibition of Nano-Metal Oxides on Bromate Formation during Ozonation Process. *Ozone-Sci. Eng.* **2014**, *36*, 549–559. [[CrossRef](#)]
28. Wen, G.; Pan, Z.-H.; Ma, J.; Liu, Z.-Q.; Zhao, L.; Li, J.-J. Reuse of sewage sludge as a catalyst in ozonation—Efficiency for the removal of oxalic acid and the control of bromate formation. *J. Hazard. Mater.* **2012**, *239–240*, 381–388. [[CrossRef](#)] [[PubMed](#)]
29. Chen, W.; Zhang, Z.; Li, X.; Wu, D.; Xue, Y.; Li, L. Reducing DBP's formation in chlorination of Br-containing Diclofenac via Fe-Cu-MCM-41/O₃ peroxidation: Efficiency, characterization DBP's precursors and mechanism. *J. Taiwan Inst. Chem. Eng.* **2018**, *84*, 212–221. [[CrossRef](#)]
30. Allard, S.; Nottle, C.E.; Chan, A.; Joll, C.; von Gunten, U. Ozonation of Iodide-Containing Waters: Selective Oxidation of Iodide to Iodate with Simultaneous Minimization of Bromate and I-THM's. *Water Res.* **2013**, *47*, 1953–1960. [[CrossRef](#)]
31. Xue, Y.; Tang, Y.; Li, X.; Chen, W.; Wu, Y.; Che, G.; Li, L. Bromate Inhibition during Ozonation of Bromide-Containing Water by the Presence of Mn Incorporated MCM-41. *J. Mater. Sci. Eng.* **2018**, *7*, 460. [[CrossRef](#)]
32. Tan, X.; Wan, Y.; Huang, Y.; He, C.; Zhang, Z.; He, Z.; Hu, L.; Zeng, J.; Shu, D. Three-dimensional MnO₂ porous hollow microspheres for enhanced activity as ozonation catalysts in degradation of bisphenol A. *J. Hazard. Mater.* **2017**, *321*, 162–172. [[CrossRef](#)]
33. Chen, W.; Li, X.; Tang, Y.; Zhou, J.; Wu, D.; Wu, Y.; Li, L. Mechanism insight of pollutant degradation and bromate inhibition by Fe-Cu-MCM-41 catalyzed ozonation. *J. Hazard. Mater.* **2018**, *346*, 226–233. [[CrossRef](#)]
34. Pinkernell, U.; von Gunten, U. Bromate minimization during ozonation: Mechanistic considerations. *Environ. Sci. Technol.* **2001**, *35*, 2525–2531. [[CrossRef](#)]
35. Yang, J.; Li, J.; Dong, W.; Ma, J.; Yang, Y.; Li, J.; Yang, Z.; Zhang, X.; Gu, J.; Xie, W.; et al. Enhancement of bromate formation by pH depression during ozonation of bromide-containing water in the presence of hydroxylamine. *Water Res.* **2017**, *109*, 135–143. [[CrossRef](#)]

36. Fischbacher, A.; Löppenberg, K.; von Sonntag, C.; Schmidt, T.C. A New Reaction Pathway for Bromite to Bromate in the Ozonation of Bromide. *Environ. Sci. Technol.* **2015**, *49*, 11714–11720. [[CrossRef](#)]
37. Huang, X.; Deng, Y.; Liu, S.; Song, Y.; Li, N.; Zhou, J. Formation of bromate during ferrate(VI) oxidation of bromide in water. *Chemosphere* **2016**, *155*, 528–533. [[CrossRef](#)]
38. Nie, Y.; Li, N.; Hu, C. Enhanced inhibition of bromate formation in catalytic ozonation of organic pollutants over Fe–Al LDH/Al₂O₃. *Sep. Purif. Technol.* **2015**, *151*, 256–261. [[CrossRef](#)]
39. Xie, L.; Shang, C.; Zhou, Q. Effect of Fe(III) on the bromate reduction by humic substances in aqueous solution. *J. Environ. Sci.* **2008**, *20*, 257–261. [[CrossRef](#)]
40. Sui, M.; Sheng, L.; Lu, K.; Tian, F. FeOOH catalytic ozonation of oxalic acid and the effect of phosphate binding on its catalytic activity. *Appl. Catal. B: Environ.* **2010**, *96*, 94–100. [[CrossRef](#)]
41. Kasprzyk-Hordern, B.; Ziótek, M.; Nawrocki, J. Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. *Appl. Catal. B: Environ.* **2003**, *46*, 639–669. [[CrossRef](#)]
42. Nie, Y.; Hu, C.; Yang, L.; Hu, J. Inhibition mechanism of BrO₃[−] formation over MnOx/Al₂O₃ during the catalytic ozonation of 2,4-dichlorophenoxyacetic acid in water. *Sep. Purif. Technol.* **2013**, *117*, 41–45. [[CrossRef](#)]
43. Radhakrishnan, R.; Oyama, S.T.; Chen, J.G.; Asakura, K. Electron transfer effects in ozone decomposition on supported manganese oxide. *J. Phys. Chem. B* **2001**, *105*, 4245–4253. [[CrossRef](#)]
44. Li, W.; Gibbs, G.V.; Oyama, S.T. Mechanism of ozone decomposition on a manganese oxide catalyst. 1. In situ Raman spectroscopy and ab initio molecular orbital calculations. *J. Am. Chem. Soc.* **1998**, *120*, 9041–9046. [[CrossRef](#)]
45. Li, W.; Oyama, S.T. Mechanism of ozone decomposition on a manganese oxide catalyst. 2. Steady-state and transient kinetic studies. *J. Am. Chem. Soc.* **1998**, *120*, 9047–9052. [[CrossRef](#)]
46. Xing, S.T.; Hu, C.; Qu, J.H.; He, H.; Yang, M. Characterization and reactivity of MnOx supported on mesoporous zirconia for herbicide 2,4-D mineralization with ozone. *Environ. Sci. Technol.* **2008**, *42*, 3363–3368. [[CrossRef](#)] [[PubMed](#)]
47. Yang, H.; Yang, S.; Wu, L.; Liu, W. Ce_xZr_{1-x}O₂ mixed oxides applied to minimize the bromate formation in the catalytic ozonation of a filtered water. *Catal. Commun.* **2011**, *15*, 99–102. [[CrossRef](#)]
48. Chao, P. Role of Hydroxyl Radicals and Hypobromous Acid Reactions on Bromate Formation during Ozonation. Ph.D. Thesis, Arizona State University, Tempe, AZ, USA, December 2002.
49. Parrino, F.; Camera-Roda, G.; Loddo, V.; Palmisano, G.; Augugliaro, V. Combination of ozonation and photocatalysis for purification of aqueous effluents containing formic acid as probe pollutant and bromide ion. *Water Res.* **2014**, *50*, 189–199. [[CrossRef](#)]
50. Nawrocki, J.; Kasprzyk-Hordern, B. The efficiency and mechanisms of catalytic ozonation. *Appl. Catal. B: Environ.* **2010**, *99*, 27–42. [[CrossRef](#)]
51. von Gunten, U.; Pinkernell, U. Ozonation of bromide containing drinking waters: A delicate balance between disinfection and bromate formation. *Water Sci. Technol.* **2000**, *41*, 53–59. [[CrossRef](#)]
52. Nie, Y.; Hu, C.; Li, N.; Yang, L.; Qu, J. Inhibition of bromate formation by surface reduction in catalytic ozonation of organic pollutants over β-FeOOH/Al₂O₃. *Appl. Catal. B: Environ.* **2014**, *147*, 287–292. [[CrossRef](#)]
53. Chitrakar, R.; Makita, Y.; Sonoda, A.; Hirotsu, T. Fe–Al layered double hydroxides in bromate reduction: Synthesis and reactivity. *J. Colloid Interface Sci.* **2011**, *354*, 798–803. [[CrossRef](#)]
54. Zhang, Y.; Xia, Y.; Li, Q.; Qi, F.; Xu, B.; Chen, Z. Synchronously degradation benzotriazole and elimination bromate by perovskite oxides catalytic ozonation: Performance and reaction mechanism. *Sep. Purif. Technol.* **2018**, *197*, 261–270. [[CrossRef](#)]
55. Zhang, T.; Hou, P.; Qiang, Z.; Lu, X.; Wang, Q. Reducing bromate formation with H⁺-form high silica zeolites during ozonation of bromide-containing water: Effectiveness and mechanisms. *Chemosphere* **2011**, *82*, 608–612. [[CrossRef](#)]
56. Gounden, A.N.; Singh, S.; Jonnalagadda, S.B. Non-catalytic and catalytic ozonation of simple halohydrins in water. *J. Environ. Chem. Eng.* **2019**, *7*, 102783. [[CrossRef](#)]
57. Song, R.; Donohoe, C.; Minear, R.; Westerhoff, P.; Ozekin, K.; Amy, G. Empirical modelling of bromate formation during ozonation of bromide containing waters. *Water Res.* **1996**, *30*, 1161–1168. [[CrossRef](#)]
58. Siddiqui, M.; Amy, G. Factors Affecting DBP Formation during Ozone-Bromide Reactions. *J. AWWA* **1993**, *85*, 63–72. [[CrossRef](#)]

59. Haag, W.R.; Hoigne, J. Ozonation of bromide-containing waters: Kinetics of formation of hypobromous acid and bromate. *Environ. Sci. Technol.* **1983**, *17*, 261–267. [[CrossRef](#)]
60. Qi, S.; Mao, Y.; Lv, M.; Sun, L.; Wang, X.; Yang, H.; Xie, Y.F. Pathway fraction of bromate formation during O₃ and O₃/H₂O₂ processes in drinking water treatment. *Chemosphere* **2016**, *144*, 2436–2442. [[CrossRef](#)] [[PubMed](#)]
61. Kishimoto, N.; Nakamura, E. Bromate Formation Characteristics of UV Irradiation, Hydrogen Peroxide Addition, Ozonation, and Their Combination Processes. *Int. J. Photoenergy* **2012**, *2012*, 10. [[CrossRef](#)]



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