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# Bromate formation control by enhanced ozonation: A critical review

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ABSTRACT

In the past two decades, ozone-based advanced oxidation processes, known as enhanced ozonation processes (EOPs), have been extensively investigated for the removal of emerging organic contaminants in water, such as pesticides, endocrine-disrupting compounds, and pharmaceuticals. EOPs offer an advantage by producing highly oxidizing radicals, such as hydroxyl radicals, to oxidize recalcitrant organic compounds. Although the EOPs are able to effectively remove emerging contaminants, several studies reported the formation of bromate, which has drawn significant attention because of its potential carcinogenicity. This issue becomes challenging for the utilization of EOPs on bromide containing water. Therefore, this work critically reviews and summarizes the mechanisms, influencing factors, advantages and disadvantages, and control strategies for bromate formation by four EOPs, i.e., peroxone and e-peroxone, photolytic ozonation, heterogeneous ozonation, and sonolytic ozonation. Various economic and technical characteristics of EOPs were also compared. Mathematical modeling, pilot and full-scale data, and secondary pollutant potential (toxic metals leaching from catalyst) have been identified as knowledge gaps, and future research should seek to address these issues.
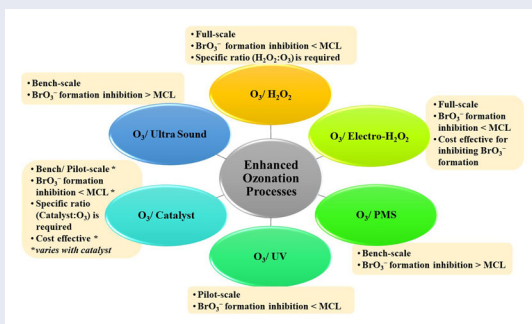
Abbreviations: AMT: amitrole; Br^-: bromide; $Br^\bullet$: bromine radical; BrO: bromine oxide; BrO^-: hypobromite ion; $BrO^\bullet$: bromine oxide radical; BrO_2^-: bromite; BrO_3^-: bromate; $BrO_2^\bullet$: bromium dioxide; Br_2O: dibromine monoxide; BZA: benzotriazole; $CaCO_3$: calcium carbonate; $Ce(NO_3)_3$: cerium nitrate; CeO_2: cerium dioxide; $Ce_xZr_{1-x}O_2$: cerium-zirconium mixed oxide; Ce-MCM-48: cerium integrated MCM-48 (mobil composition of matter); CD: catalyst dose; DBPs: disinfection by-products; DOC: dissolved organic carbon; DP: diphenhydramine; e-peroxone: electro-peroxone; Fe(II): ferrous ions; Fe(0): zerovalent iron; FeOOH: iron (III) oxide-hydroxide; α-FeOOH: goethite; β-FeOOH: akaganeite; γ-FeOOH: lepidocrocite; Fe_2O_3: ferric oxide; GAC: granular activated carbon; HEEB: high-energy electron beam; HA: humic acid; HAAs: haloacetic acids; HOBr: hypobromous acid; H_2O_2: hydrogen peroxide; O_3/H_2O_2: peroxone; H_2O_2/UV: hydrogen peroxide/

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ultraviolet irradiation; LaFeO$_3$: lanthanum ferric hydroxide; LaCoO$_3$: lanthanum cobalt hydroxide; LDH: layered double hydroxide; MCL: maximum contaminant level; MCM: mobil composition of matter; MIB: methylisoborneol; MnO$_x$/Al$_2$O$_3$: manganese oxide supported on alumina; Mn-MCM-41: MCM-41 modified with manganese; MTBE: methyl *tert*-butyl ether; nano-TiO$_2$:: nano-titanium dioxide; nano-SnO$_2$: nano-tin dioxide; NOM: natural organic matter; NH$_3$-N: ammonium; $^{\bullet}$OH: hydroxyl radical; O$_3$: ozone; O$_2$: oxygen; OH$^-$: hydroxide; O$_3$/CeO$_2$: ozonation in the presence of cerium dioxide; O$_3$/MgO: ozonation in the presence of magnesium oxide; O$_3$/FeOOH: ozonation in the presence of iron (III) oxide-hydroxide; PMS: peroxymonosulfate; O$_3$/PMS: ozonation in the presence of peroxymonosulfate; PZ: phenazone; Ru(IV): ruthenium; Si/Ce: silica/cerium; SO$_3^{2-}$: sulfite ions; SO$_4^{\bullet-}$: sulfate ion; THMs: trihalomethanes; TOC: total organic carbon; UV: ultraviolet; US: ultrasound; O$_3$/US: sonozone; O$_3$/UV: photolytic ozonation; USEPA: United States Environmental Protection Agency; VUV: vacuum ultraviolet; WHO: World Health Organization; XRD: X-ray powder diffraction; Zr: zirconium; ZrOCl$_2$: zirconyl chloride; 2,4-D: 2,4-dichlorophenoxyacetic acid

1. Introduction

The ozonation process has long been employed in drinking water treatment facilities. Besides its use for disinfection, ozone (O$_3$) is also applied to remove taste- and odor-causing compounds, and organic and inorganic contaminants. However, for conventional ozonation, due to low hydroxyl radical ($^{\bullet}$OH) yields from O$_3$ decomposition in water plus the scavenging of $^{\bullet}$OH by background constituents such as dissolved organic matter and carbonates, relatively high specific O$_3$ doses ($\geq$ 1 mg O$_3$/mg dissolved organic carbon (DOC)) are required to produce sufficient $^{\bullet}$OH to gain acceptable treatment performance. The high specific O$_3$ doses increase not only the energy demand for water treatment, but also the risk of significant bromate (BrO$_3^-$) formation if the water contains bromide ($>$ 50 µg L^{-1}) (Yao et al., 2017).

In addition to the higher O$_3$ dosage requirement and risk involved, the increasing number of emerging contaminants, such as pesticides, endocrine-disrupting compounds, and pharmaceuticals, found in raw water sources has led water utilities and researchers to seek alternative technologies to address this issue. In the past two decades, applications of ozone-based advanced oxidation processes (AOPs) or enhanced ozonation processes (EOPs) for the removal of emerging contaminants have been investigated extensively (Ghanbari et al., 2020; Khan et al., 2020; Wang et al., 2020). EOPs include combinations of ozone with another oxidant (e.g. peroxone, O$_3$/H$_2$O$_2$ or O$_3$ + persulfates), light irradiation (e.g. O$_3$/ultraviolet (UV)), ultrasound (US) (e.g. sonozone, O$_3$/US), or catalysts (e.g. catalytic ozonation, O$_3$/solid catalyst) (Lu et al., 2015; Nie et al., 2015; Wang et al., 2014; Wen et al., 2018; Zhao et al., 2013). These processes generate

hydroxyl radicals, and sulfate radicals (generated from O_3 + persulfate), which are active oxidative species that are more powerful than molecular ozone (Matilainen & Sillanpää, 2010; Sharma et al., 2018; Wang & Chen, 2020). EOPs have gained significant attention because of their ability to oxidize or completely mineralize recalcitrant organic contaminants, which is not achievable via ozonation alone. Moreover, the potential of retrofitting existing ozonation processes at water treatment facilities makes the use of EOPs a feasible option.

Although EOPs are efficient for the degradation of organic contaminants, undesired by-products are produced, particularly bromate (BrO_3^-) from the oxidation processes, thus limiting their applications (von Gunten, 2018). Bromate is a well-known by-product of ozone and ozone-based EOPs. Bromate concentrations ranging from 0.4 to 60 µg L^{-1} were reported in ozonated bromide-containing water (Butler et al., 2005). Since bromate is categorized as a suspected human carcinogenic compound, the maximum contaminant level (MCL) for bromate in drinking water is 10 µg L^{-1} in several countries (Jin et al., 2006; European Economic Commission, 1998; Health Canada, 2016; US EPA, 2006). Therefore, bromate formation is an important aspect to be considered when applying EOPs.

Although several studies have reported the contaminant degradation efficiencies of EOPs, along with inhibition of BrO_3^- formation (Chen et al., 2018; Ikehata, 2019; Khan et al., 2020; Wang et al., 2020; Wang & Bai, 2017; Zhang et al., 2018), there have been studies that were dedicated to investigating BrO_3^- formation under different EOPs (Huang et al., 2016; Li, Lu et al., 2015; Li, Shen et al., 2015; Nie et al., 2013, 2014, 2015; Wang et al., 2016; Wen et al., 2018; Wu et al., 2014; Yang, Dong, Jiang, Wang et al., 2019). A recent peer-reviewed article summarized the occurrence, mechanism, influencing factors, risk assessment, and control strategies in four oxidation processes (ozone, chlorine, sulfate and ferrate-based) involved in BrO_3^- formation (Yang, Dong, Jiang, Wang et al., 2019). However, the bromate formation and control strategies under EOPs including O_3/H_2O_2, O_3/UV, and O_3/US were only briefly touched on (Yang, Dong, Jiang, Wang et al., 2019). According to the knowledge of the authors, so far no peer-reviewed publication has comprehensively reviewed the inhibition of BrO_3^- formation under the following EOPs:

1. Chemical oxidation (Peroxone or e-peroxone: O_3/H_2O_2, and combined peroxymonosulfate (PMS) and ozone: O_3/PMS),
2. Photochemical oxidation (Photolytic ozonation: O_3/UV),
3. Heterogeneous catalysis ($O_3/Solid$ catalysts), and
4. Sonozone (O_3/US).

This article provides a critical review of different established and emerging EOPs based on data compiled during an extensive literature study. The review aims to derive an understanding of how these different oxidation processes catalyze the prevention of BrO_3^- formation in drinking water. The review summarizes the mechanisms and factors known to influence the inhibition of BrO_3^- formation under different EOPs. Additionally, the efficiencies of EOPs, versus ozonation alone, in controlling the BrO_3^- formation are compared, followed by conclusions and future perspectives.

2. Bromate formation

BrO_3^- can be formed by ozonation and EOPs via different pathways. Typically, bromide (Br^-) in water gets oxidized by O_3 or $^\bullet OH$ and is eventually transformed to BrO_3^- following different pathways (Figure 1) (Galey et al., 2001; Song et al., 1997; Symons & Zheng, 1997). In the past, BrO_3^- formation was proposed to occur via three major pathways: direct, direct-indirect, and indirect-direct (Figure 1). In the first pathway, the direct ozonation pathway, O_3 consecutively oxidizes Br^- to aqueous bromine (HOBr/OBr^-) and then to BrO_3^-. Bromate formation is more favorable at a high pH because of more abundant OBr^- (pK$_a$ HOBr/OBr^- = 8.8-9.0) (von Gunten, 2003b). Additionally, ozone reacts with OBr^- more readily ($100 \, M^{-1} \, s^{-1}$) compared to HOBr ($0.013 \, M^{-1} \, s^{-1}$). In the second pathway, the direct–indirect pathway, O_3 oxidizes Br^- to HOBr/OBr^- followed by $^\bullet OH$ oxidation of HOBr/OBr^- to $BrO^\bullet$, which disproportionates to bromite (BrO_2^-). Bromite is then oxidized by O_3 to form BrO_3^-. In the third BrO_3^- formation pathway, the indirect–direct pathway, Br^- is first oxidized by $^\bullet OH$ to form $Br^\bullet$, which is further oxidized by molecular O_3 to form $BrO^\bullet$. $BrO^\bullet$ then disproportionates to BrO_2^-, followed by O_3 oxidation to BrO_3^- (Song et al., 1997). For the direct-indirect and indirect-direct pathways, hydroxyl radicals contribute more extensively than O_3 toward BrO_3^- formation (Moslemi et al., 2014). The rates of OBr^- and HOBr oxidation (to BrO_3^-) by $^\bullet OH$, $4.5 \times 10^9 \, M^{-1} \, s^{-1}$ and $2 \times 10^9 \, M^{-1} \, s^{-1}$, respectively, are much faster than O_3 reaction rates with HOBr/OBr^- (von Gunten & Hoigné, 1994). Hence, additional BrO_3^- might be generated if $^\bullet OH$ is formed in excess during the EOP (Gottschalk et al., 2009).

A new pathway for BrO_3^- formation has quite recently been unveiled, as shown in Figure 1 (Fischbacher et al., 2015). Unlike the major pathways, which utilize oxygen transfer (O_3 to O_2) to convert BrO_2^- to BrO_3^-, the newly suggested pathway utilizes electron transfer (O_3 to O_3^-) for the same conversion. During the electron transfer process, intermediates are formed before BrO_3^- production: $BrO_2^- \rightarrow BrO_2^\bullet \rightarrow Br_2O_4 \rightarrow BrO_3^-$ (Fischbacher et al., 2015). The pathway has been reviewed and verified by several studies
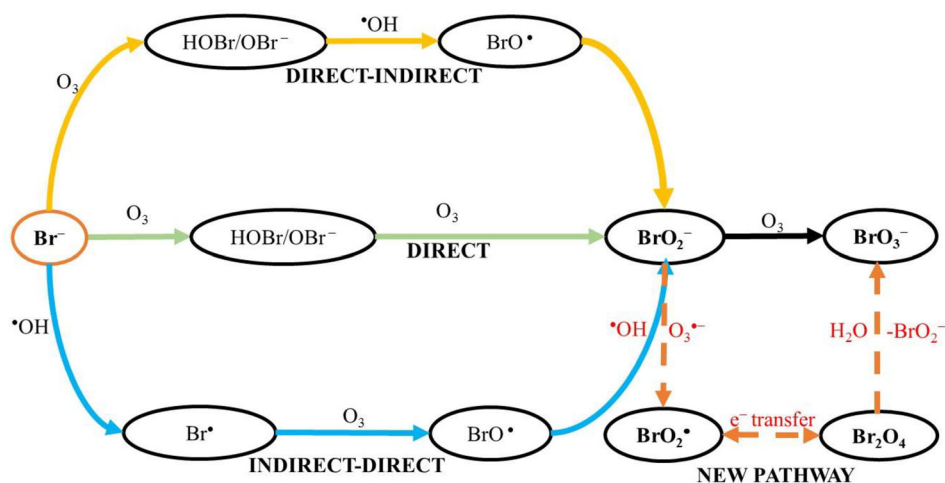
Figure 1. Bromate formation pathways and a new recommended pathway (Adapted from Song et al., 1997 and Fischbacher et al., 2015).

(Chen et al., 2018; Hull et al., 2019; Ruffino & Zanetti, 2020; von Gunten, 2018; Yang, Dong, Jiang, Wang et al., 2019).

Bromate formation during ozonation significantly depends on ozone doses and source water characteristics. These characteristics include initial Br^- concentration, solution pH, the concentration of bicarbonate, the presence of co-existing ions (such as phosphate, chloride, sulfate, silicate) and the presence of natural organic matter (NOM) (Yang, Dong, Jiang, Liu et al., 2019). Table 1 summarizes the factors influencing BrO_3^- formation. Among these factors, Br^- concentration and ozone dose are the two main factors. Typically, BrO_3^- becomes problematic for water containing greater than 50 µg L^{-1} of Br^-. In addition, ozone dose needs to be kept in a certain range. For example, at an ozone dose of two standard liters per minute, or ozone concentration $\times$ contact time (CT) between 0.31 and 2.85 mg-min L^{-1}, BrO_3^- concentration did not exceed the MCL (Wert et al., 2017).

As mentioned earlier, the pH of the water determines HOBr/OBr$^-$ ratio and availability of $^\bullet$OH to oxidize bromine species along each pathway involving indirect oxidation. Lower pH may shift the HOBr/OBr$^-$ equilibrium toward HOBr and decrease the molar ratio of $^\bullet$OH to O_3, thus directly reducing the BrO_3^- formation (Pinkernell & von Gunten, 2001). Lower pH was reported to assist HOBr and brominated organic formations, whereas higher pH assisted OBr$^-$ and BrO_3^- formations (Glaze et al., 1993). Natural organic matter also influences BrO_3^- formation. It decreases the BrO_3^- formation by scavenging $^\bullet$OH more aggressively than HOBr/OBr$^-$ (Westerhoff et al., 1998). Legube et al. (1993) reported that O_3 reacts with Br^- and OBr$^-$ slower than with NOM. Hence, when ozonated, waters

Table 1. Factors affecting BrO$_3$−formation.

	Ozone dose	Bromide concentration	Solution pH	Alkalinity Bicarbonate/Carbonate	Ammonia	Natural organic matter
BrO$_3$− yield	Increases with increase in oxidant dosage	Decreases with increasing Br− levels if oxidants are insufficient	Increases with increase in pH	Decreases with increase in bicarbonate	May decrease the BrO$_3$− formation	Decreases BrO$_3$− formation and results in the formation of organic brominated byproducts
Operating conditions and water quality *	O$_3$: 0–0.5 mg L^{-1} O$_3$: 1 mg mg^{-1} DOC	Br− < 50 µg L^{-1}	pH < 6–7	Alkalinity > 50 mg L^{-1}	NH$_3$–N: 0.03–0.14 mg L^{-1}	Br−: DOC ratio: 0.05
Mechanism	In the course of BrO$_3$− formation, the oxidants are involved in multistep reactions, including the oxidation of Br− Br and BrO$_2$−, respectively.	Increase in the initial Br− level inhibits further oxidation of HOBr/OBr to BrO$_3$− in the presence of insufficient oxidants.	Higher pH enhances the reactions of O$_3$ with •OH and other unprotonated species to generate •OH, which favors the formation of BrO$_3$−.	Bicarbonate is demonstrated to be a scavenger for •OH. Hydroxyl radicals serve as an essential oxidant for BrO$_3$− formation during ozonation. Thus, bicarbonate typically plays an inhibiting role in the oxidation of Br− or bromine by •OH, and thus decreases the formed BrO$_3$− during ozonation.	Ammonia interferes with the BrO$_3$− formation chain by reacting with HOBr, the decisive intermediate of the BrO$_3$− formation mechanism, thereby inhibiting BrO$_3$−.	In the presence of NOM, BrO$_3$− is mainly formed via the radical-involved pathways. The electrophilic compounds in NOM can react with O$_3$, leading to a reduction in O$_3$ exposure, hence decreasing BrO$_3$−. Most of the NOM can scavenge •OH, inhibiting its role in BrO$_3$− formation. Also, HOBr/OBr can also be scavenged by some of the NOM to form organic brominated byproducts and reduce BrO$_3$− formation.
References	Ratpukdi et al. (2011); Liu et al. (2012)	von Gunten (2003b); Aljundi (2011)	Lu et al. (2015); Yang et al. (2017)	Hofmann and Andrews (2006); Li et al. (2011)	Hofmann and Andrews (2001); Wert et al. (2007)	Audenaert et al. (2010); Heeb et al. (2014)

containing higher organic carbon concentrations have less BrO_3^- formation (Legube et al., 1993).

Several BrO_3^- control techniques, before and after its formation, have been investigated. Table 2 briefly compares the advantages and disadvantages associated with various methods employed in BrO_3^- abatement before and after formation. Although BrO_3^- removal technologies exist (ion exchange, membrane separation, biological reduction to bromide, and chemical reduction to bromide), these methods require additional treatment units, which would increase the cost substantially (Yang, Dong, Jiang, Wang et al., 2019). In practice, preventing BrO_3^- formation in the first place makes more sense and is widely accepted by water utilities. Therefore, these BrO_3^- control strategies must focus on minimizing the concentrations of critical reactants (i.e. O_3, $^\bullet OH$, and $HOBr/BrO^-$) in the water being treated (Elovitz & von Gunten, 1999; Song et al., 1997).

Among BrO_3^- control strategies, it was reported that only pH suppression and ammonia addition are feasible for water treatment and can reduce up to 50% of bromate formation (von Gunten, 2003b). Ammonia interferes with the BrO_3^- formation chain by converting HOBr to Br^-, thereby inhibiting BrO_3^-. However, there are chemical costs associated with these practices. Furthermore, ammonia addition may affect ozone demand, and its residual may promote nitrification in the distribution system (Hofmann & Andrews, 2007). Tables 1 and 2 provide additional information on how ammonia addition affects BrO_3^- formation.

3. Bromate formation mitigation

3.1. Bromate formation mitigation by peroxone (O_3/H_2O_2) and combined peroxymonosulfate and ozone (O_3/PMS)

The addition of hydrogen peroxide (H_2O_2) during ozonation (the peroxone process) has been identified as an appealing practice because H_2O_2 can reduce $HOBr/BrO^-$ to Br^-, thus minimizing the BrO_3^- formation (Katsoyiannis et al., 2011; von Gunten, 2003b; von Gunten & Hoigné, 1994). Moreover, the reaction between H_2O_2 and O_3 produces $^\bullet OH$, which can oxidize most organics rapidly (Acero et al., 2001; Katsoyiannis et al., 2011). Hence, enhanced pollutant degradation occurs during the ozonation of water in the presence of H_2O_2 by producing more $^\bullet OH$ compared to ozonation alone (Arvai et al., 2012; Gerrity et al., 2011; Katsoyiannis et al., 2011; Ozekin et al., 1998; von Gunten & Hoigné, 1994; Wang et al., 2014). On the other hand, production of $^\bullet OH$ from the reaction between H_2O_2 and O_3 can also enhance the formation of BrO_3^- via the indirect/direct and direct/indirect pathways (Hofmann & Andrews, 2006; Song et al., 1997).

Table 2. Advantages and disadvantages associated with different methods employed in the abatement of BrO_3^-.

Methods	Advantages	Disadvantages
BrO_3^- abatement before formation:		
pH suppression: (pH < 7 prior to ozonation)	• When pH is reduced to 7 or below, OBr_2 reduces, followed by BrO_3^- concentration reduction (Haag & Hoigné, 1983). • Hydroxyl radical production decreases with a reduction in pH, thus limiting the BrO_3^- production via the $^•OH$ pathway (Elovitz et al., 2000). • Ozone, besides being more stable at lower pH, requires reduced dosages of O_3 to achieve disinfection (Kruithof et al., 1993).	• Lowering the pH retards the $^•OH$ production, which eventually reduces the rate of pollutant degradation (Siddiqui & Amy, 1993). • Depressed pH forms HOBr, which on reacting with NOM produces brominated organics such as cyanogen bromide (Siddiqui & Amy, 1993). • Problems such as corrosion and DBP formation may arise from techniques employed in reducing the pH for controlling the BrO_3^- formation (Pinkernell & von Gunten, 2001).
Ammonia addition	• BrO_3^- formation is inhibited when ammonia reacts with HOBr, a critical intermediate in the BrO_3^- formation process (von Gunten, 2003a).	• The addition of ammonia can inhibit only a limited amount of BrO_3^- effectively. Excess dosage of ammonia does not enhance inhibition efficiency (Pinkernell & von Gunten, 2001). • Bromate formation inhibition efficiency fluctuated between 0-30% with the addition of ammonia and resulted in inconsistent BrO_3^- reduction (Siddiqui et al., 1995). • Bromamines in the presence of O_3 produce nitrate and Br^-, which catalyze the oxidation of ammonia (Haag et al., 1984). • Ammonia can get nitrified to nitrate, whereas Br^- released from bromamines may react with O_3 or $^•OH$ again, to produce BrO_3^-. Both nitrate and BrO_3^- formation affect water quality (Gillogly, 2001). • Disinfection efficiency was affected when ammonia was added during ozonation to inhibit BrO_3^- formation (Ozekin et al., 1998; Siddiqui & Amy, 1993).
BrO_3^- abatement after formation:		
Activated carbon filtration	• Significant removal of BrO_3^- was reported on increasing the activated carbon dosage. Different kinds of carbon reduce BrO_3^- concentration via different adsorption-reduction ability (Siddiqui, Amy, Ozekin et al., 1994). • About 50% of BrO_3^- concentration was reduced in a span of 10 and 20 min via activated carbon filtration, without adding any external electron donor (Kirisits et al., 2001).	• Effective BrO_3^- removal was reported with virgin granular activated carbon (GAC) only (Lefebvre et al., 1995; Legube, 1996). • Several factors affected the efficiency of GAC, including carbon-specific surface, solution pH, NOM presence, and other anions, as well as competition for active sites (Bao et al., 1999; Kirisits et al., 2001; Siddiqui, Amy, Ozekin et al., 1994). • Denitrification reactors are unsuitable for achieving BrO_3^- reduction because they require long retention times for the reactions to occur. To achieve drinking water

Table 2. Continued.

Methods	Advantages	Disadvantages
		quality that is biologically safe, posttreatment will be required (Hijnen et al., 1999). • Microbial growth on the activated carbon media is affected by changes in water quality parameters, which consequently affects the efficiency of BrO_3^- removal. For instance, when nitrate concentration reduced and dissolved oxygen concentration increased, BrO_3^- removal by biologically activated carbon reduced (von Gunten, 2003b).
UV irradiation	• UV irradiation under a wavelength range of 180-300 nm produces a large number of free radicals and species in the excited state (Mills et al., 1996).	• In the presence of NOM, free radicals are readily consumed by organic matter, thus reducing the efficiency of BrO_3^- removal by UV irradiation (Siddiqui, Amy, Ozekin et al., 1994). • Using UV irradiation only for BrO_3^- formation reduction is not cost-effective unless it targets the removal of other contaminants or DBPs as well.
High-energy electron beam (HEEB) irradiation	• Bromate can be reduced to Br^- when the water is irradiated with HEEB because it produces reducing and oxidizing species. The oxidizing species such as $^\bullet OH$ assist in the BrO_3^- abatement process (Siddiqui, Amy, Ozekin et al., 1994).	• HEEB irradiation is an expensive technique, which makes it a non-lucrative method when focusing on BrO_3^- removal only. It will be economical if more contaminants can be removed via the HEEB irradiation method.
Ru(IV) oxide	• The powdered form of Ru(IV) oxide suspended in water act as microelectrodes, wherein redox reactions occur readily, such as BrO_3^- becoming reduced to Br^- and water becoming oxidized to oxygen (Mills & Meadows, 1995).	• Investigated only at the lab scale so far (Mills & Meadows, 1995).
Chemical reducing agents: [sulfite ions (SO_3^{2-}), ferrous ions (Fe(II)), zerovalent iron (Fe(0))]	• Ferrous ions, while being oxidized, reduced BrO_3^- to Br^-; however, the dosage of ferrous ions and solution pH strongly affected the degree of BrO_3^- reduction (Gordon et al., 2002; Siddiqui, Amy, Zhai et al., 1994). • Zerovalent iron was investigated under multiple conditions and successfully reduced BrO_3^- to Br^- (Xie & Shang, 2007). Besides being efficient, it may be an economical method for BrO_3^- reduction, as well (Westerhoff & Johnson, 2001).	• The addition of sulfite ions was ineffective at reducing BrO_3^- formation and may contribute to biological growth in the distribution system (Gordon et al., 2002). • Dissolved oxygen and BrO_3^- compete with available ferrous ions, which leads to an inefficient reduction of BrO_3^- (von Gunten, 2003b). • Clarification and filtration processes may be affected due to the presence of oxidized ferric hydroxide particles (Henderson et al., 2001).

The formation of $^\bullet OH$ by peroxone is much faster than the formation of BrO_3^- by direct oxidation with O_3 (Knol et al., 2015). Bromate formation can ideally be constrained by fast O_3 decomposition and increasing the

ratio between H_2O_2 and O_3. Since H_2O_2 decreases the O_3 exposure and quenches the intermediate for BrO_3^- formation (e.g., $HOBr/BrO^-$) via the direct pathway (Figure 1), the peroxone process can effectively alleviate BrO_3^- formation (von Gunten, 2018). During the peroxone process, the residual concentration of H_2O_2 in the treated water should be maintained at or below $0.5\,mg\,L^{-1}$ in order to stay in compliance with the United States Environmental Protection Agency's standards (Chromostat et al., 1993; Paillard, 1994). If excessive H_2O_2 is used for the peroxone process in drinking water systems, biologically activated carbon filters need to be installed to quench the H_2O_2 to below $0.5\,mg\,L^{-1}$ (Dotson et al., 2010; Liu et al., 2003; Urfer & Huck, 1997). The efficiency of the peroxone process in oxidizing organic compounds can be affected by the solution pH, temperature, and contaminant type, as well as reactions that consume $^\bullet OH$, and the lower solubility of O_3 in water (Buxton et al., 1988; Hernandez et al., 2002). Table 3 presents a comparison of BrO_3^- control by O_3 and the peroxone process for different source waters.

Wang et al. (2014) highlighted a possibility to control the formation of BrO_3^- while enhancing the removal of odorants (dimethyl trisulfide and 2-methylisoborneol) by adding H_2O_2 to an ozonation process. They were able to suppress BrO_3^- formation ($<2\,\mu g\,L^{-1}$) and achieved complete removal of odor by dosing $2.0\,mg\,L^{-1}$ of O_3, while maintaining the O_3/H_2O_2 at a ratio of 0.5 (w/w). Their study suggested that a suitable H_2O_2 dose should be determined according to the raw water quality and O_3 dose (Wang et al., 2014). von Gunten et al. (1996) found that the peroxone process provided better removal of contaminants, such as atrazine, than O_3 alone in a full-scale water treatment plant. At the same O_3 dosage range ($0.8-1.5\,mg\,L^{-1}$), less BrO_3^- formation was observed in the peroxone process compared to O_3 alone. The removal of atrazine was 75% and 42% by O_3/H_2O_2 ($0.5\,mg/1.6\,mg$) and O_3 alone, respectively (von Gunten et al., 1996). Bromate in water treated by O_3/H_2O_2 was $4\,\mu g\,L^{-1}$, while it was $19\,\mu g\,L^{-1}$ for O_3 alone. It was suggested that this was due to the reduction of HOBr by H_2O_2/HO_2^- to Br^-. In addition, the shorter lifetime of O_3 in the presence of H_2O_2 hinders the formation of $BrO^\bullet$ through the reaction of $Br^\bullet$ with O_3 (von Gunten et al., 1996). Liang et al. (1999) investigated the oxidation of methyl-t-butyl ether (MTBE) by peroxone and reported that by increasing the O_3 and H_2O_2 doses from 0.7 and $2.0\,mg\,L^{-1}$ to 1.3 and $4.0\,mg\,L^{-1}$, respectively, MTBE removal increased from 54% to 87%; however, the BrO_3^- concentration increased from 8 to $83\,\mu g\,L^{-1}$.

It is important to note that several studies employing O_3/H_2O_2 reported mixed results of BrO_3^- formation. A few studies reported that the addition of H_2O_2 amplified BrO_3^- formation (Croué et al., 1996; Myllykangas et al., 2000; Siddiqui & Amy, 1993), while others have observed reductions in

BrO_3^- formation (Daniel et al., 1993; von Gunten & Oliveras, 1998). These mixed results could be due to differences in water quality. Typically, high Br^- (> 100 µg L^{-1}), H_2O_2/O_3 ratios (> 0.2 mg mg^{-1}), pH (> 9.0), and temperatures (>20 °C) increase BrO_3^- formation, whereas increasing alkalinity tends to decrease BrO_3^- formation (for example, alkalinities of 0.3, 0.8, and 1.4 mmol L^{-1} corresponding to BrO_3^- of 13, 11, and 9.4 µg L^{-1}, respectively) (Myllykangas et al., 2000). Researchers acknowledged that BrO_3^- formation can be inhibited by the presence of H_2O_2, which stimulates the reduction of $HOBr/BrO^-$ to Br^-. Therefore, the inhibition of BrO_3^- formation can be influenced by the O_3 decomposition rate, $^\bullet OH$ concentration, and $HOBr/BrO^-$ concentration (Croué et al., 1996; Siddiqui et al., 1995; von Gunten & Oliveras, 1998).

Qi et al. (2016) assessed the contributions of BrO_3^- formation by the three different pathways (direct, direct-indirect, and indirect-direct) in O_3 and O_3/H_2O_2 systems. Bromate formation was mainly from the indirect-direct pathway during the peroxonation of a surface water sample (Yellow River, China). The Yellow River sample contained 140 µg L^{-1} Br^-, 3.4 mg L^{-1} dissolved organic carbon (DOC), 0.04 cm^{-1} UV absorbance at 254 nm, 746 µS cm^{-1} electrical conductivity, 98 mg L^{-1} Cl^-, 240 mg L^{-1} as $CaCO_3$ hardness, and 125.3 mg L^{-1} as $CaCO_3$ alkalinity. On increasing the H_2O_2 dosage during the peroxone process, unlike the indirect-direct pathway wherein increased formation of BrO_3^- was observed, the direct and direct-indirect pathways reduced the BrO_3^- formation. The transformation of Br^- to BrO_3^- initially increased and eventually decreased to its minimum (5.1%) when the peroxone (O_3/H_2O_2) ratio was at 1.5. At the same ratio, the highest fraction of Br^- was converted to BrO_3^- (64.0%) via the indirect-direct pathway, suggesting that $^\bullet OH$ scavengers were useful for controlling BrO_3^- formation. Based on the characteristics of water, a specific ratio of $O_3:H_2O_2$ is desired to control BrO_3^- formation.

Another method for BrO_3^- formation control, by limiting O_3 exposure (O_3 dose $\times$ CT) as a linear relationship between the exposure and bromate formation, was identified (Guo et al., 2020). Compared to other techniques discussed in this review, the O_3/H_2O_2 process is the most investigated and implemented. Hence, the use of the O_3/H_2O_2 process has regulatory acceptance and a history of proven full-scale operation.

The electro-peroxone process or e-peroxone process is similar to peroxonation except that H_2O_2 is generated in situ from cathodic O_2 reduction (Figure 2). During this process, O_2 is converted to H_2O_2 electrochemically, which further generates $^\bullet OH$ by reacting with O_3 (peroxone process). Since the e-peroxone process can be automated, it allows the process to be monitored and controlled via a supervisory control and data acquisition system, saving the time and energy needed in a manual process operation. Existing

Table 3. Comparison of bromate control by ozone and peroxone.

Water sources and tested conditions	O_3 or O_3/H_2O_2 dosage (mg L^{-1})	BrO_3^- formation (µg L^{-1})	Micropollutants oxidized	Removal Efficiency (%)	Reference
Colorado River Water pH = 6.5, DOC = 116.6 mgL^{-1}, alkalinity = 312 mgL^{-1} as CaCO$_3$, Br$^-$ = 90 µg L^{-1}	4 4/1.3	68 28	MTBE	33 79	Liang et al. (1999)
Lake Zurich water (Zurich, Switzerland) pH = 7, DOC = 1.4 mg L^{-1}, alkalinity = 205 mg L^{-1} as CaCO$_3$, Br$^-$ = 50 µg L^{-1}	2 2/0.7 4/1.4	15.1 8.8 16.8	MTBE	39 46 71	Acero et al. (2001)
Well water Porrentruy (Porrentruy, Switzerland) pH = 7, DOC = 0.8 mg L^{-1}, alkalinity = 410 mg L^{-1} as CaCO$_3$, Br$^-$ = 50 µg L^{-1}	2 2/0.7 4/1.4	20.7 12.5 33.5	MTBE	28 37 65	
Lake Murten (Murten, Switzerland) pH = 7, DOC = 2.7 mg L^{-1}, alkalinity = 311 mg L^{-1} as CaCO$_3$, Br$^-$ = 17.6 µg L^{-1}	2 2/0.4 2/0.2	25 6 6.2	MTBE	33 34 46	Arvai et al. (2012)
Pre-treated Meuse River (Berghambacht, Netherlands) pH = 7.97, DOC = 4.26 mg L^{-1}, NH$_3$= < 0.02 mg NH$_4^+$L^{-1}, DOC = 4.23 mg L^{-1}, alkalinity = 143.44 mg L^{-1} as CaCO$_3$, Br$^-$ = 119 µg L^{-1}	1.5/6	0.41	Bentazone Phenazone Furosemide Diclophenac Bromocil Trimethoprim Carbamazepine Isoproturon Metformin Atrazine Iopromide Diglyme Ibuprofen Metoprolol	>95% > 90% 24% 40 % 52 % 57 % 73 % 80 %	Knol et al. (2015)
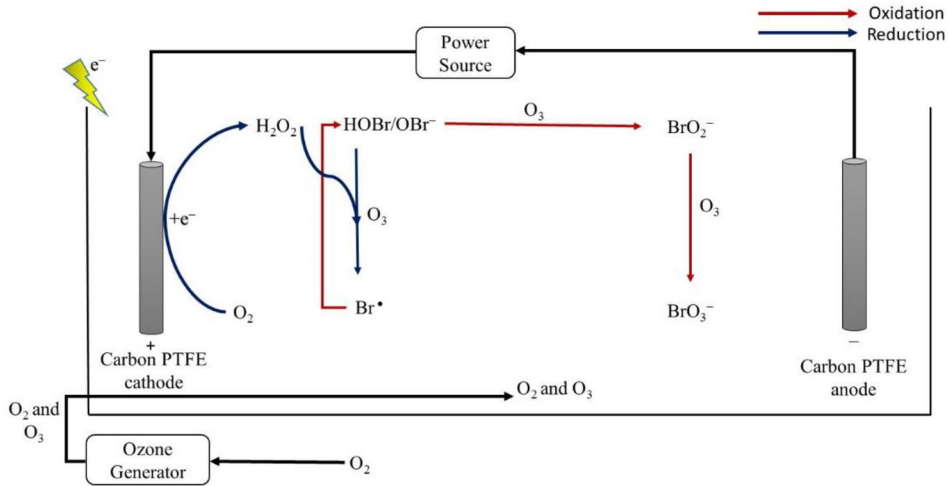
Figure 2. In situ electro-generated H_2O_2 reduces the BrO_3^- formation using the electro-peroxone process (e-peroxone process) (Adapted from Li, Shen et al., 2015).

peroxone process in treatment plants can be modified into e-peroxone process. In situ generation of H_2O_2 avoids the risks associated with the transportation and storage of H_2O_2. The cost of H_2O_2 generation by electricity was lower than the cost of H_2O_2 stocks (Yao et al., 2018). Unlike other catalytic processes, no chemicals and catalysts are required for e-peroxone. Furthermore, the use of nontoxic and stable carbon-based electrodes can eliminate the issue of secondary pollutants, such as toxic metal ions from catalysts (Guo et al., 2020).

Although e-peroxone can effectively inhibit BrO_3^- formation, it reduces the O_3 concentration in the solution. This may reduce the disinfection benefit of O_3 that is observed in the conventional peroxone process (von Gunten, 2003b). It is possible to set up the system to perform ozonation first for disinfection, followed by the e-peroxone process, but more research would be needed to identify the optimal working conditions to achieve both disinfection and BrO_3^- formation inhibition (Li, Shen et al., 2015). Previous studies on the e-peroxone process were conducted on laboratory and pilot scales (Li, Shen et al., 2015; Wang et al., 2018). Therefore, scaling-up the process to provide sufficient amounts of H_2O_2 for full-scale water treatment plants could be a challenge (Wang et al., 2018). Other issues, such as requirements for additional infrastructure, as well as energy consumption for H_2O_2 production, need to be considered for practical application.

Li, Shen et al. (2015) studied BrO_3^- formation inhibition by the e-peroxone process in comparison with ozonation. Their results indicated that for ozonation alone, the water sample containing Br^- (150 μg L^{-1}) produced

significant amounts of BrO_3^- ($\sim$60-120 µg L^{-1}) in the effluent. However, by applying a small current (60–100 mA) to electrochemically generate H_2O_2 from O_2, the e-peroxone process decreased the BrO_3^- concentration to < 10 µg L^{-1} and removed NOM significantly (DOC reduction from 2.5 to 1.0 mg L^{-1}). Thus, with the potential to control BrO_3^- formation and reduce NOM concentration during water treatment, the e-peroxone process can potentially be an effective way to improve the existing ozonation process (Li, Shen et al., 2015).

Another study (Yao et al., 2017) compared the abatement of taste- and odor-causing micropollutants (methylisoborneol and geosmin) and BrO_3^- formation between conventional ozonation and e-peroxonation of bromide containing surface waters. E-peroxone reduced methylisoborneol (MIB) and geosmin with significantly lower BrO_3^- formation than conventional ozonation (0.5–1.0 mg O_3 mg DOC^{-1}), which could not effectively reduce MIB and geosmin. Upon increasing the O_3 dose (1.0–2.5 mg O_3 mg DOC^{-1}) in conventional ozonation, although MIB and geosmin decreased, BrO_3^- formation was significant. Upon increasing the applied current (from 20 to 40 mA) during the e-peroxone process, the BrO_3^- formation dropped below the regulatory limit; however, the residual H_2O_2 needed to be removed. Thus, considering the high ozone dose requirement for reducing MIB and geosmin during accidental spills or seasonal events, e-peroxone can be employed as a contingency plan to conventional ozonation (Yao et al., 2017).

Sulfate radical-based ($SO_4^{\bullet-}$) EOPs are promising alternatives to $^{\bullet}OH$ based EOPs. Sulfate radicals are more selective to organic pollutants and less selective to water matrices than $^{\bullet}OH$ (Buxton et al., 1988; Neta et al., 1988). Peroxymonosulfate (PMS) has been applied along with ozone to generate $SO_4^{\bullet-}$ (Tan et al., 2020; Wen et al., 2018; Yang, Dong, Jiang, Wang et al., 2019). Recent studies reported that the O_3/PMS process forms both $^{\bullet}OH$ and $SO_4^{\bullet-}$ simultaneously (Equations 1–4), which enhance the removal of micro-pollutants (Tan et al., 2020; Wu et al., 2019).

$$-O_3SOO- \ + \ O_3 \rightarrow \cdot -O_3SO_5 \rightarrow \tag{1}$$

$$-O_3SO_5- \rightarrow SO_5^{\bullet-} + \ O_3^{\bullet-} \tag{2}$$

$$2SO_5^{\bullet-} \rightarrow 2SO_4^{\bullet-} + \ O_2 \tag{3}$$

$$O_3^{\bullet-} + \ H_2O \rightarrow {}^{\bullet}OH \ + \ OH^- + \ O_2 \tag{4}$$
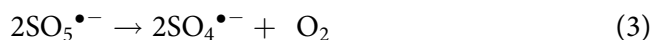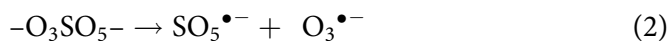
These two oxidative species ($^{\bullet}OH$ and $SO_4^{\bullet-}$) not only play roles in the degradation of target contaminants, but also contribute to BrO_3^- formation by the O_3/PMS process (when treating bromide containing water). Figure 3 presents the reaction scheme for BrO_3^- formation by $SO_4^{\bullet-}$ and HSO_5^-/SO_5^{2-}. Bromide can be directly oxidized to $HOBr/OBr^-$ by HSO_5^-/SO_5^{2-} through oxygen atom transfer reactions (Equations 5 and 6). $SO_4^{\bullet-}$ can
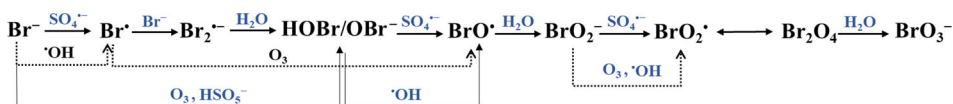
Figure 3. The reaction scheme for BrO_3^- formation via the O_3/PMS process (Adapted from Guan et al., 2020).

readily oxidize Br^- to $Br^\bullet$ (Equation 7) and HOBr/OBr$^-$ to $BrO^\bullet$, leading to BrO_3^- formation (Yang, Dong, Jiang, Wang et al., 2019) (Figure 3). The rate constant of $SO_4^{\bullet-}$ with Br^- is 10 orders of magnitude higher than that of HSO_5^-/SO_5^{2-}. Thus, the major pathway for BrO_3^- formation is from reaction with $SO_4^{\bullet-}$.

$$HSO_5^- + Br^- \rightarrow HOBr + SO_4^{2-}, \ k = 0.7 \ M^{-1}s^{-1} \tag{5}$$

$$SO_5^{2-} + Br^- \rightarrow OBr^- + SO_4^{2-}, \ k = 0.17 \ M^{-1}s^{-1} \tag{6}$$

$$SO_4^{\bullet-} + Br^- \rightarrow Br^\bullet + SO_4^{2-}, \ k = 3.5 \times 10^9 M^{-1}s^{-1} \tag{7}$$
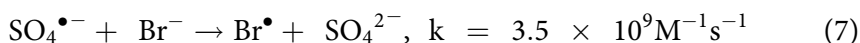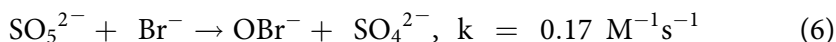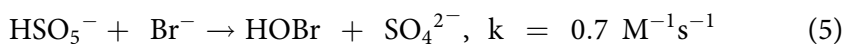
The formation of BrO_3^- by the O_3/PMS process strongly depends on PMS concentration, solution pH, and bromine species (HOBr/OBr$^-$). Wen et al. (2018) investigated the formation of BrO_3^- by O_3/PMS and ozone alone in distilled and real water samples. In distilled water, O_3/PMS yielded higher BrO_3^- formation compared to O_3 alone. BrO_3^- increased substantially from 3.97 to 10.57 μM as the PMS dose increased from 0 to 100 μM. At 200 and 300 μM 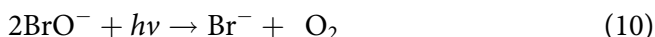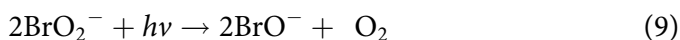of PMS, the BrO_3^- formation appeared to slowly increase to 11.74 and 12.60 μM, respectively. Wen et al. (2018) reported that the enhanced BrO_3^- formation with increasing the PMS dose was analogous to ozone utilization efficiencies, which were 19.8, 25.8, 27.8, 30.4, 30.7, and 34.5% at PMS dosages of 0, 5, 50, 100, 200, and 300 μM, respectively. The higher ozone utilization efficiency promoted the production of oxidative species ($^\bullet$OH and $SO_4^{\bullet-}$), which were responsible for BrO_3^- formation. The radical scavenging experiments (using methanol for quenching $SO_4^{\bullet-}$ and $^\bullet$OH and tertiary-butanol for quenching $^\bullet$OH) confirmed that both $^\bullet$OH and $SO_4^{\bullet-}$ were involved in BrO_3^- formation (Wen et al., 2018). At low pH (pH 4), BrO_3^- formation was limited regardless of the concentration of PMS. This was due to low ozone decomposition to $^\bullet$OH, low production of $SO_4^{\bullet-}$, and high abundance of HOBr ($pK_a = 8.8$). An increase of pH also resulted in an increase of BrO_3^- formation by O_3/PMS. The higher proportion of $^\bullet$OH and OBr$^-$ at high pH, along with PMS species (HSO_5^-/SO_5^{2-}, $pK_a = 9.4$) contributed by the generation of $SO_4^{\bullet-}$, promotes BrO_3^- formation. At pH > 10, PMS species is in a dianionic form (SO_5^{2-}). Yang et al. (2015) suspected that mostly the dianionic form (SO_5^{2-}), rather than the monoanionic form (HSO_5^-), reacted with ozone to produce $SO_4^{\bullet-}$ (Equations 1–3).

For a real water sample, BrO_3^- formation by O_3/PMS was 5 to 9% less than for distilled water (Wen et al., 2018). This was due to the presence of radical scavengers, such as NOM and carbonate species. Similar to the case of O_3 alone, the addition of NH_4^+ reduced BrO_3^- formation in the real water sample treated by O_3/PMS. Wen et al. (2018) reported that an increase of NH_4^+ concentration reduced BrO_3^- formation. NH_4^+ at $400\,\mu g\,L^{-1}$ was enough to inhibit the formation of bromate in the real water sample. Another approach for BrO_3^- inhibition for the O_3/PMS process is by adding low doses of carbon materials. Wen et al. (2020) investigated the application of low dosages (5-60 mg L^{-1}) of powdered activated carbon (PAC), carbon nanotubes (CNT), and graphene oxide (GO) for the inhibition of BrO_3^- formation and the improvement of oxalic acid degradation by O_3/PMS. Among the three carbon materials, GO provided the best result for BrO_3^- inhibition and organic compound degradation. For 10 mg L^{-1} of PAC, CNT, and GO, the bromate conversion efficiency (25.1%) was reduced to 15.9%, 14.1%, and 8.8%, respectively at pH = 7.0 and 50 μM of PMS. These carbon materials were found to reduce HOBr/OBr$^-$ to Br$^-$ (Wen et al., 2020), and therefore inhibited BrO_3^- formation. The highest performance by GO might be due to its higher specific surface area and mesopore volume, which provide more reaction sites. It was assumed that the defects (zigzag/armchair edges) and carbonyl and carboxyl functional groups in GO were the active sites for HOBr/OBr$^-$ reduction (Wen et al., 2020).

3.2. Bromate formation mitigation by photolytic ozonation (O_3/UV)

Several studies have investigated the mitigation of BrO_3^- formation under different UV irradiation conditions (Peldszus et al., 2004; Phillip et al., 2006; Ratpukdi et al., 2011; Siddiqui et al., 1996; Zhao et al., 2013). Photolytic ozonation produces $^\bullet$OH via H_2O_2/UV, O_3/H_2O_2, and O_3/OH$^-$ (high pH) reaction routes, as shown in Figure 4. Photolytic ozonation with UV forms H_2O_2, a precursor for the production of $^\bullet$OH. Although the degradation of O_3 leads to the production of $^\bullet$OH, both pathways, direct (involving O_3) and indirect (involving $^\bullet$OH), contribute to BrO_3^- formation. In the O_3/UV process, the photolytic consumption of dissolved O_3 by UV leads to a lower residual O_3 concentration, and in turn less BrO_3^- formation. In addition, BrO_3^- can partially be reduced to BrO_2^-, then BrO^-, and eventually Br$^-$ by absorbing photons from UV irradiation (Equations 8–10) (Siddiqui et al., 1996).

$$2BrO_3^- + h\nu \rightarrow 2BrO_3^- + O_2 \qquad (8)$$

$$2BrO_2^- + h\nu \rightarrow 2BrO^- + O_2 \qquad (9)$$

$$2BrO^- + h\nu \rightarrow Br^- + O_2 \qquad (10)$$
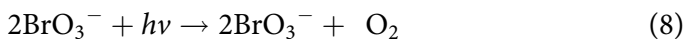
The efficiency of the O_3/UV process in mitigating BrO_3^- formation is influenced by several parameters (UV intensity, O_3 dosage, pH, wavelength, UV dose, types of UV lamps, and organic matter), as discussed in detail below.
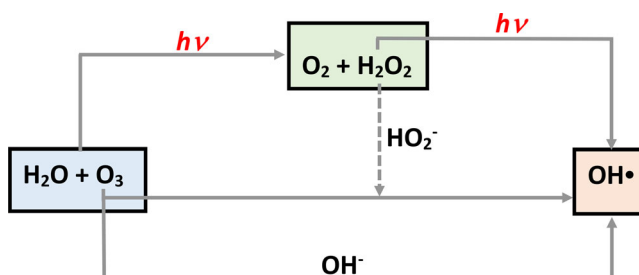
Figure 4. Hydroxyl radical production routes in the O_3-UV process (Modified from Oh et al., 2005).

Ratpukdi et al. (2011) studied the effects of UV intensity, O_3 dosage, and pH on the BrO_3^- formation of coagulated surface water. Their study compared the formation of BrO_3^- among O_3, O_3-UV, and O_3-vacuum-UV (VUV) processes. Among the three processes, O_3-VUV (185 nm + 254 nm) produced the least amount of BrO_3^- compared to O_3 and O_3-UV (254 nm), which produced four and six times more BrO_3^-, respectively. Ozone dosage played an important role in the BrO_3^- formation by the O_3-VUV process. When raising the O_3 dosage from 1 to 2 and 4 mg O_3 mg DOC^{-1} with 120 W of VUV power at pH 7, an increase of around 64 and 213% in BrO_3^- concentration was observed. Additionally, increases in VUV power and pH amplified the BrO_3^- formation due to more abundant $^\bullet OH$ (from water homolysis by VUV) and more OBr^-, respectively. The purpose of the O_3-VUV process was to remove organic matter from the water. Their study suggested that achieving both the drinking water requirements for BrO_3^- concentration and mineralization of organic matter could be challenging (Ratpukdi et al., 2011).

Previous studies indicated that the presence of organic matter led to UV absorption and eventually reduced the removal efficiency of BrO_3^- (Phillip et al., 2006; Siddiqui et al., 1996). However, Zhao et al. (2013) reported that for O_3/UV, BrO_3^-, formation decreased with increasing the humic acid (HA) concentration. Ozone preferentially reacted with HA over Br^-, due to its higher reaction rate constant, thus inhibiting BrO_3^- formation. Bromate formation by O_3 + UV irradiation from a low-pressure mercury lamp (emitting 254 nm and 185 nm) in the presence and absence of HA was studied by Zhao et al. (2013). A low O_3 dose of 2 mg L^{-1} was generated by the UV irradiation, whereas O_3 doses higher than 2 mg L^{-1} were generated by an ozone generator (silent electric discharge). In the absence of HA, BrO_3^- concentrations during the O_3/UV process (17.1–77.6 µg L^{-1}) were 2.1–2.9 times more than the concentrations generated by the O_3 process (8.0–33.8 µg L^{-1}), when O_3 doses ranging from 2 to 21 mg L^{-1} were continuously applied. In the presence of HA, 2 mg L^{-1} of O_3 (generated by

the UV irradiation) reduced BrO_3^- to less than $10\,\mu g\ L^{-1}$ (at $4\,mg\ L^{-1}$ DOC, $1.4\,\mu g\ L^{-1}$ BrO_3^- was formed). The study also reported that BrO_3^- formation increased in both O_3/UV and O_3 processes when the Br^- concentration was raised; however, the increase in BrO_3^- formation at higher pH was observed with the O_3 process only.

UV/VUV radiation, when used in small doses in the presence of O_3, reduces the formation of BrO_3^-. Less BrO_3^- formation is observed with VUV (compared to UV), at low pH and low O_3 dosages (Ratpukdi et al., 2011). Supplementing UV reduces the requirement of O_3. An increase in the O_3 dose can increase the production of free $^\bullet OH$, thereby increasing the BrO_3^- formation. Therefore, the O_3 dosing must be monitored regularly. Although organic matter (NOM, HA) consumes O_3, and in turn limits its BrO_3^- formation, it absorbs UV, thus reducing BrO_3^- removal efficiency by UV. Overall, O_3/UV is not widely applied in practice because it is too costly.

3.3. Bromate formation mitigation by heterogeneous catalytic ozonation

Enhanced ozonation by metals can be categorized as homogeneous or heterogeneous based on the type of metal (catalyst). Dissolved metal ions activate O_3 in a homogeneous catalytic ozonation process, whereas solid catalysts (metals/metal oxides) are responsible for activating the O_3 during a heterogeneous catalytic ozonation process (Kasprzyk-Hordern et al., 2003). There has been more research on heterogeneous catalytic ozonation compared to homogeneous catalytic ozonation, particularly in relation to BrO_3^- formation inhibition. In addition, the recovery of metal ions (as homogeneous catalysts) in the water treatment process can be challenging. Hence, this section focuses exclusively on heterogeneous catalytic ozonation. Some of the solid catalysts include metal oxides (MnO_2, TiO_2, Al_2O_3), and metals or metal oxides on metal oxide supports (e.g. Cu/Al_2O_3, Cu/TiO_2, Ru/CeO_2, TiO_2/Al_2O_3, Fe_2O_3/Al_2O_3) (Huang et al., 2005). Heterogeneous catalytic ozonation is a potential method to reduce BrO_3^- formation with limited chemical additions (because catalysts are retrievable and reusable after reactions) and lower energy requirements (no external source of energy is required for employing the catalyst, unlike other enhanced techniques such as O_3-UV, sonozone, and electroperoxone processes).

Although catalytic ozonation by several heterogeneous catalysts is effective for the degradation of organic contaminants and inhibition of BrO_3^- formation, the technology lacks full-scale applications for several reasons. Wang and Chen (2020) and Nawrocki and Kasprzyk-Hordern (2010) comprehensively reviewed several shortcomings of heterogeneous catalytic

ozonation, including how and why the technology did not progress beyond laboratory-scale. One of the main reasons is that a dominant mechanism governing the catalytic process has not been elucidated. Whether O_3 decomposition to form surface-bound or free radicals, or the adsorption of organics on a catalyst surface plays a superior role on the catalytic process is unclear. Several other questions that remain unanswered include but are not limited to: How is O_3 oxidized (directly or indirectly) on the catalyst surface? What are the roles of different chemical components in water (such as carbonates, bicarbonates, sulfates, phosphates, and fluorides) on catalytic activity? What factors influence the catalytic performance? (Nawrocki & Kasprzyk-Hordern, 2010). In addition, issues such as catalyst separation and recycling, reactor design, and proper mixing, along with the leaching of dissolved metal from the catalyst into the aqueous solution, add to challenges associated with the heterogeneous catalytic ozonation technology (Wang & Chen, 2020).

There are three possible mechanisms for catalytic ozonation in heterogeneous systems: 1) the chemisorption of O_3 on the catalyst surface, causing the production of active species, which react with organic compounds adsorbed on the surface; 2) the chemisorption of organic compounds on the catalyst surface, which react with the O_3 present in aqueous or gaseous form; and/or 3) the chemisorption of both O_3 and organic compounds on the catalyst surface, followed by reactions between the two adsorbed species (Kasprzyk-Hordern et al., 2003). The surface properties of the catalyst and the pH of the solution dictate the efficiency of the heterogeneous catalytic ozonation process. These factors influence the properties of surface active sites, as well as the O_3 decomposition reactions (Kasprzyk-Hordern et al., 2003).

For heterogeneous catalytic ozonation, the selected catalyst must be analyzed for its chemical and physical characteristics, such as its purity, surface area, porosity, density, mechanical strength, pore size distribution, and pore volume. These variables are important in understanding the adsorption ability of a catalyst, as this is one of the important stages in the heterogeneous catalytic ozonation process. In addition, adsorption of inorganic ions can permanently block the active surface sites of the catalysts, thus reducing the catalytic activity. Therefore, these characteristics are important for evaluating the efficiency of a catalyst. Chemical properties include the occurrence of active surface sites, e.g., Lewis acid sites, which are accountable for catalytic reactions and chemical stability. During ozonation, certain solid catalysts function better (for both contaminant degradation and BrO_3^- inhibition) in the presence of another catalyst that acts as a support, such as alumina (Nie et al., 2013; 2014; 2015). Therefore, the review of heterogeneous catalytic ozonation below is categorized into two major groups: solid catalyst and solid catalyst with support (Figure 5).
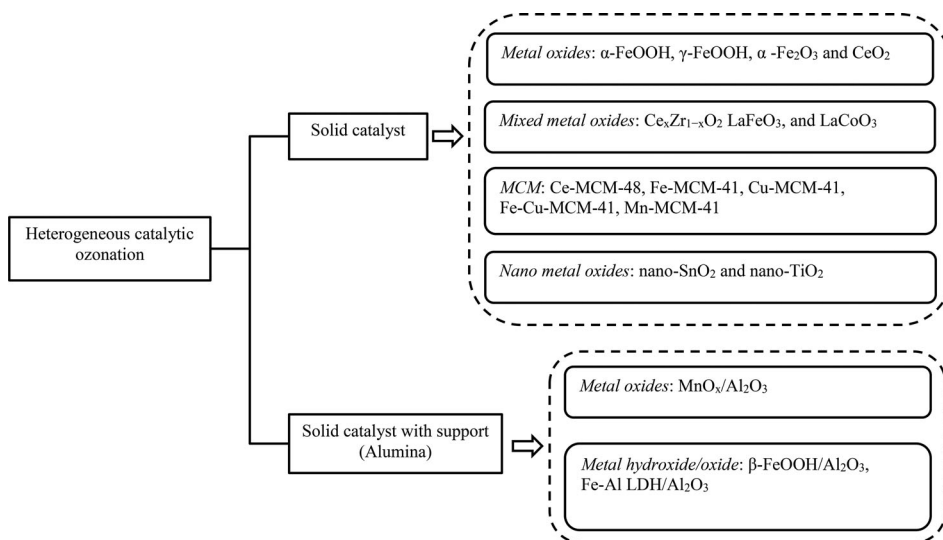
Figure 5. Heterogeneous catalysts investigated for BrO_3^- inhibition in the catalytic ozonation process.

3.3.1. Solid catalyst

3.3.1.1. Metal oxides. Metal oxide catalysts that are commonly used can be pure, mixed, or doped. BrO_3^- formation mitigation during ozonation can be achieved by adding zeolite or cerium dioxide (CeO_2) (Sagehashi et al., 2005; Zhang et al., 2008, 2011). Four metal oxides, α-FeOOH, γ-FeOOH, α-Fe$_2$O$_3$, and CeO$_2$ were tested for their effects on BrO_3^- formation potential during the ozonation of Br$^-$-containing water (Zhang et al., 2008). Catalytic ozonation with α-Fe$_2$O$_3$ was reported to generate BrO_3^-, whereas CeO$_2$ minimized the BrO_3^- formation better than the other two metal oxides (α-FeOOH, γ-FeOOH). The minimization of BrO_3^- formation during ozonation in the presence of CeO$_2$ (O$_3$/CeO$_2$) showed better results for Br$^-$ concentration less than or equal to 1.0 mg L^{-1} and at pH < 7, compared with ozonation alone.

Based on the BrO_3^- formation that involves direct ozonation, along with the $^\bullet$OH oxidation of Br$^-$ or HOBr/OBr$^-$ species, Wang et al. (2016) suggested four potential pathways for BrO_3^- inhibition by O$_3$/CeO$_2$ as follows: 1) the adsorption of Br$^-$ or BrO_3^- on the CeO$_2$ surface; 2) the reduction of BrO_3^- or HOBr/OBr$^-$ to Br$^-$ by CeO$_2$; 3) blocking of the route from Br$^-$ to HOBr/OBr$^-$ by CeO$_2$; and (4) blocking of the oxidation of HOBr/OBr$^-$ to BrO$^\bullet$. However, the first pathway was ruled out since no adsorption of Br$^-$ or BrO_3^- was found on the CeO$_2$ catalyst (Zhang et al., 2008, 2011). The Br$^-$ concentration in the O$_3$/CeO$_2$ process was similar to that in the ozone alone process, and the HOBr/OBr$^-$ concentration in O$_3$/CeO$_2$ process was higher than that in the ozone alone process. This indicated no blocking for the oxidation of Br$^-$ to HOBr/OBr$^-$ and no reduction of

HOBr/OBr$^-$ to Br$^-$, and consequently the second and third pathways were ruled out. It was deduced that the fourth pathway, blocking the oxidation of HOBr/OBr$^-$ to BrO$^\bullet$, was responsible for BrO$_3^-$ formation inhibition.

Ozone decomposition also produces $^\bullet$OH, which promotes BrO$_3^-$ formation (Figure 1). For the O$_3$/CeO$_2$ process, less $^\bullet$OH formation is expected, and this led to a decreasing oxidation rate of HOBr/BrO$^-$ to BrO$^\bullet$. Wang et al. (2016) investigated the role of $^\bullet$OH using para-chlorobenzoic acid as an $^\bullet$OH probe compound. They reported the lowest formation of $^\bullet$OH and BrO$_3^-$ under ozonation with CeO$_2$ compared to magnesium oxide (MgO) and synthetic goethite (FeOOH). It was suggested that O$_3$ adsorbed on the active sites of the CeO$_2$ and was decomposed to active oxygen species (e.g., superoxide, ozonide, and surface oxygen atom) rather than $^\bullet$OH (Bulanin et al., 1998). Table 4 presents case studies of bromate control by various catalytic ozonation processes and other EOPs.

Another possibility for mitigating BrO$_3^-$ formation is by introducing ferrate(VI) during the ozonation process (O$_3$/[FeO$_4$]$^{2-}$), as reported by Han et al. (2013). A dosage of 2.0 mg L^{-1} of ferrate(VI) was required to completely inhibit the BrO$_3^-$ formation when the initial Br$^-$ concentration was from 100 to 200 µg L^{-1}, with pH 3.0 to 9.0, and temperatures of 5 to 40 °C, while keeping the O$_3$ dosage between 1.5 and 2.5 mg L^{-1}. In addition, under the same conditions, when the Br$^-$ concentration was increased from 200 to 500 µg L^{-1}, a higher ferrate(VI) dosage of 5.0 mg L^{-1} was used, wherein the BrO$_3^-$ concentration increased, but was still below the MCL (Han et al., 2013). Huang et al. (2016) found that the production of BrO$_3^-$ exceeded the MCL when Br$^-$ was oxidized by ferrate(VI) in the absence of phosphate and under a moderately weak acidic condition. They reported that in the presence of phosphate, more H$_2$O$_2$ was generated, which could reduce HOBr (produced from reaction between Fe(VI) and Br$^-$), thus inhibiting the BrO$_3^-$ formation. More research data would be helpful in determining the optimum value of ferrate as a catalyst for BrO$_3^-$ control, as well as the associated costs.

BrO$_3^-$ can be inhibited completely with ferrate(VI) addition to ozonation. Compared to other methods that could inhibit BrO$_3^-$ formation, ferrate(VI) is advantageous because low dosages are required, and it is less sensitive to water characteristics. However, the catalyst performance has only been confirmed with batch studies so far (Han et al., 2013; Huang et al., 2016). Besides, ferrate(VI), BrO$_3^-$ formation can be significantly inhibited by CeO$_2$ due to the surface reduction of BrO$^\bullet$ to HOBr/OBr$^-$. However, the active sites on CeO$_2$ surface require restoration of the lost catalytic activity after use (Wang et al., 2016; Zhang et al., 2008). As the synthesis cost for the CeO$_2$ catalyst is high, this technique is not considered cost effective.

Table 4. Recent case studies on bromate control using enhanced ozonation techniques.

Enhanced ozonation techniques	Test conditions	BrO_3^- formation with O_3 (μgL^{-1})	BrO_3^- formation with Enhanced ozonation (μgL^{-1})	Enhanced ozonation BrO_3^- removal efficiency (%)	References
Photolysis (UV)	$Br^- = 100\ \mu g\ L^{-1}$, pH = 7, $O_3 = 2\ mg\ L^{-1}$, t = 60 min	7.6	2.1	61.6	Zhao et al. (2013)
Mixed metal oxides ($Ce_{0.75}Zr_{0.25}O_2$)	$Br^- = 290\ \mu g\ L^{-1}$, pH = 8.1, catalyst dose (CD) = 100 mg L^{-1}, $O_3 = 3\ mg\ L^{-1}$, T = 20±1°C, alkalinity = 125.3 mg L^{-1} as $CaCO_3$, t = 20 min	>40	~20	53	Yang et al. (2011)
Manganese oxide/Alumina (MnO_x/Al_2O_3)	$Br^- = 100\ \mu g\ L^{-1}$, pH = 6.5, CD = 0.25 g L^{-1}, $O_3 = 2\ mg\ L^{-1}$, 2,4-D = 10 mg L^{-1}, t = 10 min	2.25	0.5	>90	Nie et al. (2013)
Iron oxide hydroxide/Alumina (β-FeOOH/Al_2O_3)	$Br^- = 125\ \mu g\ L^{-1}$, pH = 6.0, CD = 0.25 g L^{-1}, $O_3 = 2\ mg\ L^{-1}$, t = 40 min	21.5	0	~100	Nie et al. (2014)
Layered double hydroxide/Alumina (Fe-Al LDH/Al_2O_3)	$Br^- = 125\ \mu g\ L^{-1}$, pH = 8.0, CD = 0.25 g L^{-1}, $O_3 = 2.0\ mg\ L^{-1}$, alkalinity = 190 mgL^{-1} as $CaCO_3$, t = 60 min, 2,4-D = 10mgL^{-1}	76.74	<12.79	~100	Nie et al. (2015)
MCM-Modified (Ce_x-MCM-48) MCM-41	$Br^- = 1000\ \mu g\ L^{-1}$, pH = 7.5, CD = 0.5 g L^{-1}, $O_3 = 2.0\pm0.1\ mgL^{-1}$, T = 25±1°C, t = 30 min $Br^- = 1000\ \mu g\ L^{-1}$, pH = 5, CD = 1 g L^{-1}, $O_3 = 50\ mg\ Hr^{-1}$, T = 25°C, t = 60 min	<200 432.5	Ce_{66}-MCM-48 ≤ 20, Ce_{200}-MCM-48 = ~40, Ce_{100}-MCM-48 ≤ 25, Ce_{30}-MCM-48 ≤ 30, MCM-48 = ~40, CeO_2 ≤ 50, Cu-MCM-41 = 28.8, Fe-MCM-41 = 31.5, Fe-Cu-MCM-41 = 124.5	91, 78.6, 78.6, 78.6, 78.6, 63.9, 97, 96.8, 87.5	Li, Lu et al. (2015), Chen et al. (2018)
Nano metal oxides (TiO_2, SnO_2)	$Br^- = 400\ \mu g\ L^{-1}$, pH = 6.0, $O_3 = 3.38\ mg\ L^{-1}$, T = 26°C, t = 15 min, CD = 0.1 g L^{-1}	81.93	TiO_2 = 21.22, SnO_2 = 44.40	TiO_2 = 74.1, SnO_2 ≥ 45.8	Wu et al. (2014)
Sonolysis (Ultrasound)	$Br^- = 1000\ \mu g\ L^{-1}$, Power = 100W, pH = 7, $O_3 = 0.03 L\ min^{-1}$, t = 10 min	300	150	50	Lu et al. (2015)
Ferrate (FeO_4^{2-})	$Br^- = 200\ \mu g\ L^{-1}$, pH = 7.0, $O_3 = 2.5\ mgL^{-1}$, T = 25°C, CD = 2 mg L^{-1}	36.3	0	100	Han et al. (2013)

3.3.1.2. Mixed metal oxides. Cerium-zirconium mixed oxides ($Ce_xZr_{1-x}O_2$) have been explored as catalysts for the inhibition of BrO_3^- formation using a batch reactor (Yang et al., 2011). $Ce_xZr_{1-x}O_2$ showed a promising performance in suppressing BrO_3^- formation and reducing organic matter. Compared to pure CeO_2, $Ce_xZr_{1-x}O_2$ demonstrated more efficiency in reducing BrO_3^- formation during the ozonation process. In a study by Yang et al. (2011), $Ce_xZr_{1-x}O_2$ was developed by a co-precipitation method, wherein different molar ratios of $Ce(NO_3)_3$ and $ZrOCl_2$ were added to the ammonia solution. The surface area of $Ce_xZr_{1-x}O_2$ was more ($157.1 \, m^2 \, g^{-1}$) than pure CeO_2 ($133.6 \, m^2 \, g^{-1}$) and increased with increasing Zr in the oxides ($157.1 \, m^2 \, g^{-1}$ ($Zr_{0.1}$), $187.8 \, m^2 \, g^{-1}$ ($Zr_{0.25}$), $300.4 \, m^2 \, g^{-1}$ ($Zr_{0.5}$), and $368.5 \, m^2 \, g^{-1}$ ($Zr_{0.84}$)). Zr effectively limited the increase of CeO_2 crystallites. Yang et al. (2011) prepared different compositions of the mixed metal catalyst ($Ce_{0.9}Zr_{0.1}O_2$, $Ce_{0.75}Zr_{0.25}O_2$, $Ce_{0.5}Zr_{0.5}O_2$ and $Ce_{0.16}Zr_{0.84}O_2$) and compared their efficiencies. $Ce_{0.75}Zr_{0.25}O_2$ was found to be the most efficient catalyst in inhibiting the BrO_3^- formation because it reduced around 53% BrO_3^- formation after 20 min reaction, compared to $Ce_{0.9}Zr_{0.1}O_2$, $Ce_{0.16}Zr_{0.84}O_2$ and $Ce_{0.5}Zr_{0.5}O_2$ which reduced 44, 38, and 18% BrO_3^- formation, respectively.

The formation of BrO_3^- was restricted as the decomposition of O_3 was enhanced in the presence of the $Ce_xZr_{1-x}O_2$. In addition, the formation of $^{\bullet}OH$ was promoted by the catalyst, which allowed the $^{\bullet}OH$ to react rapidly with Br^- and other organics present in the solution. Since the oxidizing rate of $^{\bullet}OH$ is higher for organic compounds than for Br^-, $Ce_xZr_{1-x}O_2$ could block the oxidation of Br^- by O_3 decomposition, allowing the enhanced removal of organic compounds by $^{\bullet}OH$, while controlling the BrO_3^- formation. The adsorption of Br^- and BrO_3^- on the $Ce_xZr_{1-x}O_2$ surface was measured during the ozonation reaction, and no adsorption was observed, based on relatively constant Br^- and BrO_3^- concentrations in the water phase. Moreover, no metal ions were detected in the solution. Although $Ce_xZr_{1-x}O_2$ is a more effective catalyst for reducing BrO_3^- formation during ozonation than CeO_2, it is unclear why different ratios of Ce and Zr provided different BrO_3^- formation. In addition, the mechanism for the involvement of $HOBr/OBr^-$ in BrO_3^- formation requires future research.

Another group of catalysts, perovskite oxides ($LaFeO_3$, and $LaCoO_3$), was investigated for BrO_3^- formation inhibition under benzotriazole (BZA) degradation by ozone (Zhang et al., 2018). The experimental conditions were an initial Br^- concentration of $100 \, \mu g \, L^{-1}$, pH of 6.4, O_3 dose of $2 \, mg \, L^{-1}$, BZA dose of $10 \, mg \, L^{-1}$ and catalyst dose of $0.5 \, g \, L^{-1}$, reaction time of 120 min, and room temperature. $LaFeO_3$ inhibited 73% BrO_3^- formation without BZA degradation, whereas $LaCoO_3$ inhibited 71% BrO_3^-

formation with complete degradation of BZA. These two catalysts inhibited BrO_3^- formation differently. Although $LaFeO_3$ did not catalytically enhance O_3 decomposition to generate reactive oxygen species for BZA degradation, it reduced BrO_3^- efficiently. $[Fe-H_2O_2]_s$, generated from surface hydroxyl groups of $LaFeO_3$, and H_2O_2 (formed from BZA degradation) was responsible for reducing BrO_3^- to $HOBr/OBr^-$ (Zhang et al., 2018). This finding suggested that adding an $LaFeO_3$ catalyst to ozonation might only benefit BrO_3^- reduction, but not micro-pollutant removal. On the other hand, $LaCoO_3$ has higher lattice oxygen species on its surface ($O^{2-}/-OH$ ratio = 0.58) than $LaFeO_3$ ($O^{2-}/-OH$ ratio = 0.31), resulting stronger ozone decomposition and superior catalytic activity compared to $LaFeO_3$. Surface hydroxyl groups on $LaCoO_3$ promoted O_3 decomposition readily, subsequently generating more radicals, especially $^\bullet OH$, which degraded BZA and generated more H_2O_2. Finally, BrO_3^- was reduced to $HOBr/OBr^-$ by H_2O_2 (formed from BZA degradation).

BrO_3^- formation through ozonation is reduced greatly by the addition of $Ce_xZr_{1-x}O_2$ mixed metal oxides, compared to a single metal oxide. Maximum efficiency of $Ce_xZr_{1-x}O_2$ is achieved at a specific element ratio (Yang et al., 2011). However, certain factors, such as the catalyst synthesis cost, installation setup, and catalyst regeneration rate, have not been investigated. More research on both technical and commercial aspects is needed before the process can be applied practically.

3.3.1.3. Mobil composition of matter. Mobil composition of matter (MCM) is a silica based mesoporous adsorbent, which can be modified by integrating transitional metals such as Fe and Mn (Schumacher et al., 1999). The integration enhances the catalytic ability of MCM (Gómez et al., 2005; Zhao et al., 2001). A team of researchers (Li, Lu et al., 2015) investigated the inhibition of BrO_3^- formation by employing catalytic ozonation using cerium integrated MCM-48 or Ce-MCM-48 as a catalyst. This catalyst was prepared hydrothermally by integrating different ratios (30-200) of Si/Ce with MCM-48. The Si/Ce ratio of 66 (Ce_{66}-MCM-48) was reported as the most optimal ratio for the inhibition of BrO_3^- formation (76-91%) at a pH range of 6.3 to 9.5 and 15-30 °C, based on the initial Br^- concentration of 1.0 mg L^{-1}, O_3 dose of 1.1 ± 0.1 mg L^{-1}, catalyst dose of 0.5 g L^{-1}, and reaction time of 20 min. Ce_{66}-MCM-48 stimulated the O_3 decomposition to produce $^\bullet OH$, which further generated H_2O_2. The reactions involving the oxidation of Br^- and $HOBr/BrO^-$ by O_3 and $^\bullet OH$ were inhibited, thus reducing the BrO_3^- formation. During the catalytic ozonation process, refractory organics were also degraded via indirect oxidation of $^\bullet OH$. The catalytic capacity of Ce_{66}-MCM-48 was regenerated with continuous circulation of reactions between Ce(III) and Ce(IV) on its surface (Li, Lu et al., 2015).

Chen et al. (2018) investigated the performance of a MCM-41 catalyst modified with metal(s) in inhibiting BrO_3^- formation and degrading diclofenac (DCF) during catalytic ozonation. They compared the performance of O_3 alone and O_3 with the modified MCM-41, which included O_3/Fe-MCM-41, O_3/Cu-MCM-41, and O_3/Fe-Cu-MCM-41. During the experiment, 1,000 µg L^{-1} of Br^- solution (pH 5) and 20 mg L^{-1} of DCF solution (pH 7) were exposed to a catalyst dosage of 1 g L^{-1} at 298 K. Although BrO_3^- formation was inhibited by all types of O_3/MCM-41 tested, the efficiencies differed. Compared with BrO_3^- production by O_3 alone, the maximum BrO_3^- formation inhibition (93%) was observed with O_3/Cu-MCM-41 and O_3/Fe-MCM-41 followed by O_3/Fe-Cu-MCM-41 (71%), corresponding to the following BrO_3^- concentrations in treated water: 28.8 µg L^{-1} for O_3/Cu-MCM-41, 31.5 µg L^{-1} for O_3/Fe-MCM-41, 124.5 µg L^{-1} for O_3/Fe-Cu-MCM-41, and 432.5 µg L^{-1} for O_3 alone. Less BrO_3^- was generated during the catalytic ozonation process compared to ozonation alone because the catalyst consumed the ozone, thus leaving less ozone for BrO_3^- formation (Li, Lu et al., 2015).

MCM-41 was modified with manganese (Mn-MCM-41), and the effect of increasing temperature rate (0.5, 1 and 2 K min^{-1}) during calcination on BrO_3^- inhibition was investigated (Xue et al., 2018). Out of the three rates investigated, the catalyst produced at 1 K min^{-1} offered the highest BrO_3^- inhibition efficiency (96.7%), followed by those produced at 0.5 K min^{-1} (~80%) and 2 K min^{-1} (~75%). The different heating rates changed the dispersion of Mn species and the oxidation state of Mn, which is related to oxygen vacancies and active sites. The Mn-MCM-41 produced at 1 K min^{-1} had more oxygen vacancies, which could adsorb H_2O and dissociate to surface species, than the other two catalysts. O_3 easily reacted with the surface species and less O_3 exposure resulted in reduced BrO_3^- formation.

A cerium integrated mesoporous adsorbent (Ce_{66}-MCM-48) in combination with O_3 is highly efficient for BrO_3^- inhibition. Moreover, its large pore volume, strong thermal stability and high surface area increase its efficiency for BrO_3^- inhibition. Ce_{66}-MCM-48 is a cost-effective catalyst for the ozonation process. Its catalytic capability is enhanced via circulating reactions on its surface between Ce(III) and Ce(IV). The efficiency of the catalysts could be deteriorated if the specific ratio of Ce and Si is disturbed, blocking the active sites of the catalyst, and thus damaging the structure of the catalyst (Li, Lu et al., 2015).

Qiang et al. (2013) reported that O_3 catalyzed by powdered Ce-MCM-48 substantially inhibited BrO_3^- formation (> 95% inhibition efficiency compared to O_3 alone) based on a bench-scale experiment. However, separating the powdered Ce-MCM-48 in full-scale water treatment can be very challenging. This led the authors to use a granular form of Ce-MCM-48 instead

of the powdered form. A 33-day continuous pilot scale experiment demonstrated high BrO_3^- inhibition efficiency of the Ce_{66}-MCM-48 catalyst (75% average, initial Br^-: ~220 μgL^{-1}) (Qiang et al., 2013). O_3/Mn-MCM-41 also inhibits BrO_3^- formation, but the performance fluctuates with solution pH (6.5, 7.5, and 9.5), calcination temperature rate (0.5, 1, and 2 K min^{-1}), and Mn content (Mn_x-MCM-41, x = 40, 80, 100, and 120) in the catalyst (Xue et al., 2018). The calcination temperature rate affects the valence states of active Mn species, the dispersion of Mn on the catalyst, and the formation of oxygen vacancies, which could increase surface hydroxyl groups on the catalyst and accelerate O_3 degradation, resulting in less BrO_3^- formation.

Although metals or metal-oxides are commonly used during heterogeneous catalytic processes, using them without support can lead to issues, such as restricted specific surface area and inadequate active sites. Therefore, these catalysts are typically supported by meso- or micro-porous structures, such as alumina, zeolite, and activated carbon, in order to enhance mass transfer. One-dimensional, mesoporous silicates such as MCM-41 (large surface area and high porosity) were reported to significantly enhance the mineralization performance during catalytic ozonation (Chen et al., 2018). MCM-48 is a three-dimensional mesoporous silicate that has an interconnected cubic pore structure. It can facilitate dispersion of both reactants and products in an aqueous solution due to its pore structure, which is less likely to be blocked compared to MCM-41 (Li et al., 2018). However, more work is needed to gain a better perspective on the catalytic mechanism and catalyst regeneration methods, as well as the treatment capacity of MCM based catalysts, leaching of potential toxic elements, and analysis of economic feasibility of the process at water treatment plants.

3.3.1.4. Nano metal oxides. Wu et al. (2014) investigated the performance of nano-metal oxides, nano-titanium dioxide, (nano-TiO_2) and nano-tin dioxide (nano-SnO_2), as catalysts during ozonation on BrO_3^- formation, along with their catalytic mechanisms. Both nano-SnO_2 and nano-TiO_2 had the potential to reduce the formation of BrO_3^- in the presence of ozone (Table 4). O_3/Nano-TiO_2 performance on the BrO_3^- formation inhibition improved with increasing nano-TiO_2 dosage (0 to 100 mg L^{-1}) and decreasing O_3 concentration (4.62 to 2.0 mg L^{-1}), with an initial Br^- concentration (1.2 to 0.4 mg L^{-1}), and solution pH (8.0 to 6.0). The oxidation of Br^- by $^{\bullet}OH$ prevailed during the catalytic ozonation process. The generation of $^{\bullet}OH$ amplified with the disintegration of O_3 by the nano-metal oxides. The presence of $^{\bullet}OH$ led to the production of H_2O_2, which reduced HOBr/BrO^- to Br^-, thus inhibiting the BrO_3^- formation. The nano-metal oxides reduced BrO_3^- formation only
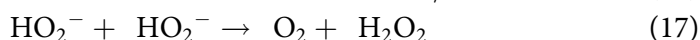
at high dosages of both O_3 (4.62 mg L^{-1}) and catalyst (100 mg L^{-1}), making the technique expensive (Wu et al., 2014).

The application of nanoparticles in water treatment can be challenging because they have to be removed. Recent studies have used TiO_2 nanoparticles embedded on textile or fabric, or nano-composite polymers with UV to degrade different organic compounds (Ahmari et al., 2016, 2018a, 2018b; Shakouri et al., 2016). These techniques could also be applied for ozonation with nano-metal oxide catalysts. Since very few studies have been published, more research is required to determine methods for regeneration of the catalyst and to identify other possible mechanisms behind the inhibition of BrO_3^- by nano-metal oxides.

3.3.2. Solid catalyst with support (Alumina)

3.3.2.1. Metal oxides. There has only been one published study on the mitigation of BrO_3^- using metal oxides as support (Nie et al., 2013). In the study, manganese oxide, supported on mesoporous Al_2O_3 (MnO_x/Al_2O_3), was applied as a catalyst to investigate the inhibition of BrO_3^- formation and the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) in the presence of ozone. The results showed that MnO_x/Al_2O_3 in the presence of O_3 could significantly control the formation of BrO_3^-.

The combination of O_3 and MnO_x/Al_2O_3 inhibited the BrO_3^- formation due to the redox reactions on the catalyst surface involving adsorption and decomposition of O_3. In the presence of MnO_x/Al_2O_3 via interfacial electron transfer, BrO_3^- was reduced to Br^-, thus inhibiting the formation of BrO_3^-. A relative UV-visible (UV-vis) absorption spectrum of MnO_x showed multivalent oxidation states of Mn (Mn^{2+}, Mn^{3+}, and Mn^{4+}). A comparison of the UV-vis absorption spectra of MnO_x and MnO_x/Al_2O_3 highlighted that the Mn^{2+} within the catalyst was responsible for the inhibition of BrO_3^- formation (Equations 15 and 16). Catalytic ozonation in the presence of MnO_x/Al_2O_3 generated 77% less BrO_3^- compared to ozonation alone, suggesting that Mn^{2+} could reduce both BrO_3^- and $HOBr/BrO^-$ to Br^-. The following reactions pertaining to BrO_3^- inhibition were proposed by Nie et al. (2013):

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \tag{11}$$

$$O_3 + HO_2 \rightarrow O_2^{\bullet-} + {}^{\bullet}OH + O_2 \tag{12}$$

$$Mn^{4+} + O_2^{\bullet-} \rightarrow Mn^{3+} + O_2 \tag{13}$$

$$Mn^{3+} + O_2^{\bullet-} \rightarrow Mn^{2+} + O_2 \tag{14}$$

$$BrO_3^- + Mn^{2+} \rightarrow Br^- + Mn^{3+}/Mn^{4+} \tag{15}$$

$$HBrO/BrO^- + Mn^{2+} \rightarrow Br^- + Mn^{3+}/Mn^{4+} \tag{16}$$

$$HO_2^- + HO_2^- \rightarrow O_2 + H_2O_2 \tag{17}$$
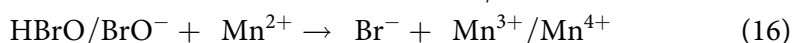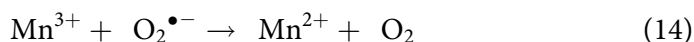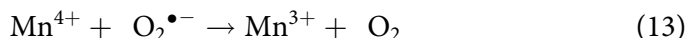
Compared to ozonation alone, the H_2O_2 concentration in the MnO_x/Al_2O_3-O_3 system was lower. For TOC (associated with 2,4-D) removal under the absence and presence of influent Br^- (100 µg L^{-1}), the catalytic ozonation was more efficient than ozonation alone, ~70 and ~55% versus 26 and 7%, respectively. The BrO_3^- formation could be reduced by almost 75% by ozonation with the MnO_x/Al_2O_3-O_3 catalyst. During the treatment, no specific ratio of manganese oxide/alumina and O_3 is required, which makes it easier for operation and monitoring (Nie et al., 2013). However, the O_3 dosage varies with the flow and chemical characteristics of the water to be treated, and hence must be calculated and monitored regularly. Similar to the mixed metal oxides, the costs for manufacturing the catalyst and its regeneration have not been investigated. Therefore, the catalyst cannot be commercially used until these attributes are fully explored.

3.3.2.2. Metal hydroxide/oxide. Compared to other ions present in water (Cl^-, OH^-), BrO_3^- showed higher adsorption and selectivity in the presence of iron (III) oxide-hydroxide or akaganeite (β-FeOOH) (Chitrakar et al., 2008; Xu et al., 2012). β-FeOOH/Al_2O_3 was employed as a catalyst for the inhibition of BrO_3^- formation during ozonation (Nie et al., 2014). In the absence of O_3, around 68% of BrO_3^- adsorbed on the β-FeOOH/Al_2O_3, whereas complete inhibition of BrO_3^- was observed in the presence of O_3. During the catalytic ozonation, BrO_3^- was transformed to Br^-. The surface Fe(II) of β-FeOOH/Al_2O_3 was accountable for the BrO_3^- formation inhibition according to the in-situ diffuse reflection UV-vis spectra. Ozone degradation in the presence of the catalyst (β-FeOOH/Al_2O_3) produced $HO_2^{•-}/O_2^{•-}$, which reacted with surface Fe(III) to generate Fe(II). This finding was confirmed by Fourier transform infrared spectroscopy and gas chromatography-mass spectrometry. In addition to the inhibition of BrO_3^- formation, TOC was also reduced by β-FeOOH/Al_2O_3 catalyzed ozonation when amitrole (AMT), diphenhydramine (DP), phenazone (PZ) or 2,4-D was present (Nie et al., 2014).

Layered double hydroxides (LDHs) are synthetic materials composed of positively charged layers of mixed metal hydroxides (Nalawade et al., 2009). LDHs have been popularly used as anion exchangers to adsorb contaminants (arsenate, nitrate, phosphate, and bromide) from aqueous solutions (Chitrakar et al., 2008; Goh et al., 2008; Palmer et al., 2009; Prasanna & Kamath, 2009; Rives, 2001). To examine the effect of organic pollutants with different structures (PZ, AMT and 2,4-D) on BrO_3^- formation mitigation during catalytic ozonation, Nie et al. (2015) employed Fe-Al layered double hydroxides (Fe-Al LDHs, the molar ratio of Fe(II) to Fe(III) of 1:10), which was supported and dispersed on mesoporous Al_2O_3. Unlike ozonation alone, Fe-Al LDHs/Al_2O_3 efficiently inhibited BrO_3^- formation

and simultaneously removed organic pollutants. Surface Fe(II) reactive species were found to be responsible for mitigating BrO_3^- formation during catalytic ozonation. Similar to β-FeOOH/Al_2O_3, Fe-Al LDHs/Al_2O_3 also inhibited BrO_3^- formation efficiently in the presence of organics during the catalytic ozonation. The three organic pollutants investigated reduced BrO_3^- formation in the following order: AMT < PZ < 2,4-D. The reaction between surface Fe(III) with $HO_2^{\bullet-}/O_2^{\bullet-}$ (contributed by organics) produced Fe(III) intermediate complex during the catalytic ozonation, which increased the generation of the Fe(II) species responsible for reducing BrO_3^-. Different rates of BrO_3^- inhibition occurred over Fe-Al LDH/Al_2O_3 when different amounts of oxygen-containing functional groups were produced during catalytic ozonation of organics. Fe-Al LDHs/Al_2O_3 was reported to be effective for BrO_3^- formation inhibition and organic removal during the catalytic ozonation (Nie et al., 2015).

Complete removal of BrO_3^- can be achieved via the surface adsorption of akaganeite, even in the presence of organic compounds. Akaganeite can degrade organic pollutants via surface adsorption, wherein the oxygen-containing functional groups of the organic pollutants react with surface Fe(III) of the catalyst generating Fe(II) and reduce the organic pollutants (Nie et al., 2014). No specific ratio is required for the use of the catalyst with O_3, thus reducing operational and monitoring efforts. However, the costs and challenges involved in the synthesis of akageneite make this catalyst less attractive. Moreover, the catalyst needs to be replenished, due to active sites being blocked after the adsorption of BrO_3^-.

A summary of the mechanisms involved in BrO_3^- inhibition by the reviewed heterogeneous catalytic ozonation processes is presented in Table 5. In addition to the BrO_3^- inhibition mechanisms, Table 5 shows the efficiency of each catalyst in removing different types of organic compounds while inhibiting BrO_3^- formation. The information in Table 5 is helpful in determining which catalyst to best use, based on the contaminants present in water.

3.4. Bromate formation mitigation by sonozone

Ultrasound in the presence of O_3, also known as sonozone (O_3/US), stimulates a combined effect, which makes it more effective than the individual effects of ozone or US. During sonozone, the transfer of O_3 to aqueous solution is enhanced by ultrasonic radiation through increasing the volumetric mass transfer coefficient. Sonication with pulses creates a vibrational disturbance in the solution that increases the specific surface area of bubbles and reduces the liquid film thickness (Zhang et al., 2007). Additionally, sonication can enhance the O_3 decomposition process, which

Table 5. Mechanisms for bromate control by heterogeneous catalytic ozonation in the presence of other organic compounds.

| Ozone/Catalyst	Removal of compounds	BrO_3^- inhibition (%)	BrO_3^- inhibition mechanisms	References
O_3/CeO_2 (Metal oxide)	Organic hydrocarbons and para-chloronitrobenzene (37.3–40.8%)	Variable up to 90+.	Inhibition of $^\bullet OH$ formation prevented BrO_3^- formation via adsorption of O_3 and O_2 on active Ce (IV) sites.	Zhang et al. (2008)
O_3/$(FeO_4)^{2-}$ (Metal oxide)	No data (BrO_3^- only)	~100	Fe intermediates could partially consume the O_3, and H_2O_2 could reduce $HBrO/BrO^-$ to Br^-. A combination of low valent Fe intermediates and H_2O_2 production was responsible for BrO_3^- inhibition.	Han et al. (2013)
O_3/ $Ce_xZr_{1-x}O_2$ (Mixed metal oxide)	UV absorbing organic compounds at 64.8%	53	$Ce_xZr_{1-x}O_2$ promoted the O_3 decomposition in the ozonation reaction, thus limiting the BrO_3^- formation pathway involving O_3 oxidation. Also, the catalyst promoted the formation of $^\bullet OH$. $Ce_xZr_{1-x}O_2$ effectively reduced BrO_3^- formation and amplified the removal of organics because they are oxidized faster than Br^-.	Yang et al. (2011)
O_3/Al_2O_3/MnO_x (Mixed metal oxide)	2,4-D (55–60%)	90	Multivalent oxidation states of Mn reduced the BrO_3^- formation to Br^- via interfacial electron transfer process.	Nie et al. (2013)
O_3/Ce-MCM-48 Mobile composition of matter	Atrazine at 67% and omethoate at 41%	91	Ce66-MCM-48 stimulated the inhibition of O_3 oxidation, leading to the production of $^\bullet OH$, which reduced the oxidation of Br^- and $HOBr/BrO^-$. Also, the circulating reactions between Ce (III) and (IV) inhibited the oxidation of Br^- and $HOBr/BrO^-$, thus inhibiting BrO_3^- formation.	Han et al. (2013)
O_3/Fe-Cu-MCM-41	Diclofenac (77.6%)	88	Lewis acid sites and Cu content increased Fe-Cu-MCM-41 catalytic activity, generating more $^\bullet OH$, leading to higher accumulation of BrO_3^-.	Chen et al. (2018)
O_3/ β -FeOOH/Al_2O_3 (Metalhydroxide)	2,4-D (64%), phenazone (33%), diphenhydramine (30%), and amitrole (14%)	~100 with 2,4-D	BrO_3^- was adsorbed on the catalyst surface and reduced by surface Fe(II). Organic compounds contributed functional groups containing oxygen, which reacted with the surface Fe(III) generating more surface Fe(II).	Nie et al. (2014)
O_3/Fe-Al LDH/Al_2O_3 (Metal hydroxide)	2,4-D > phenazone > amitrole. Increased TOC removal (82%) with catalytic ozonation compared to ozonation alone (28%)	~100	During the phenazone degradation process, BrO_3^- was partially reduced to Br^-, while a part was adsorbed by Fe(II) on the surface of a layered double hydroxide.	Nie et al. (2015)
O_3/SnO_2, O_3/TiO_2 (Nano metal oxide)	No data (BrO_3^- only)	46, 74	Nano metal oxide promoted the formation of $^\bullet OH$ generating H_2O_2, which reduced BrO_3^- via partial HOBr reduction.	Wu et al. (2014)

further leads to the production of reactive $^\bullet$OH (Destaillats et al., 2000). Compared to ozonation alone, sonozone provides stronger oxidation, as two $^\bullet$OH are formed per O_3 molecule consumed, as shown in the following equations (Adewuyi, 2005):

$$O_3 +))) \rightarrow O_2 + O \tag{18}$$

$$O + H_2O \rightarrow 2^\bullet OH \tag{19}$$

where))) refers to ultrasonic irradiation.

Researchers attributed the enhanced removal of pollutants by O_3/US to the elevated $^\bullet$OH concentration, similar to the O_3/H_2O_2 system (Ji et al., 2012; Park et al., 2012). A study by Lu et al. (2015) investigated the formation of BrO_3^- under sonolytic ozonation using batch experiments. Factors influencing BrO_3^- formation include US power, O_3 dose, O_3 flow rate, contact time, and solution pH. Increasing O_3 doses (0.5, 1.5 and 2.8 mg L^{-1}), along with increasing US power, synergized more BrO_3^- formation. BrO_3^- concentrations at all O_3 dosages increased until 66 W of the US, and then remained constant up to 100 W. This effect was more pronounced at the highest ozone dose (2.8 mg L^{-1}). For O_3/US, BrO_3^- concentrations below MCL were only observed at O_3 of 0.5 mg L^{-1} with US of 0-100 W and O_3 of 1.5 mg L^{-1} for US < 66 W. Increasing the O_3 flow rate (0.03 to 0.2 L min^{-1}) led to more BrO_3^- formation. O_3/US was found to produce higher BrO_3^- concentrations than O_3 alone (except at O_3 flow rate of 0.03 L min^{-1}). Increasing the duration (within a range of 0 to 15 min) of O_3/US treatment resulted in more BrO_3^- formation, which remained constant beyond 15 min. BrO_3^- formation increased with solution pH (based on pH 5.5, 7.0, and 9.2) for both O_3 alone and O_3/US.

Sonozone reduced BrO_3^- formation substantially in the presence of ethanol, a radical scavenger. This was because scavenging $^\bullet$OH inhibited the BrO_3^- formation pathway at $HOBr^-$ (as explained in detail in the introduction section of this review). Lu et al. (2015) further reported that bromine and its intermediates ($HOBr/BrO^-$) played an important role in BrO_3^- formation. In the presence of $HOBr/BrO^-$, the oxidation process is described as:

$$^\bullet OH + HOBr/BrO^- \rightarrow BrO^\bullet \rightarrow \ldots\ldots \rightarrow BrO_3^- \tag{20}$$
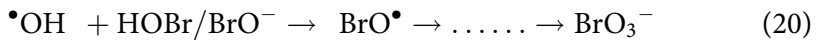
During sonozone, US transformed $HOBr^-/BrO^-$ to Br^- via the production of H_2O_2, as expressed below:

$$US \rightarrow {^\bullet OH} \text{ (bulk, aq) } \rightarrow H_2O_2 \leftrightarrow HO_2^- + H^+ \tag{21}$$

$$HOBr/BrO^- + H_2O_2/HO_2^- \rightarrow Br^- \tag{22}$$
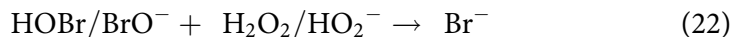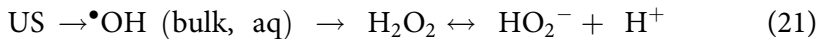
As shown in Equations 21 and 22, the increase of the H_2O_2 formation via the recombination of $^\bullet$OH limited the $HOBr/BrO^-$ conversion to

BrO_3^-. This explains less BrO_3^- formation under O_3/US compared to O_3 at low O_3 doses.

With very limited published research related to sonozone and BrO_3^- formation (Lu et al., 2015), there is not enough information to highlight and compare the pros and cons of the technique. Although sonozone can enhance the degradation of target pollutants, more studies are needed to investigate the specific O_3 flowrate, US power, and treatment period for the BrO_3^- inhibition, with varying water quality parameters. The costs of sonicator and US production, and the reliability and detailed conditions of the process to reduce BrO_3^- formation have yet to be investigated.

4. Future outlook and direction

The presence of Br^- in both surface water and groundwater brings a potential risk of generating the undesired by-product, BrO_3^-, during ozone-based water treatment. For more than two decades, BrO_3^- mitigation, along with the degradation of contaminants by EOPs, have been investigated. The most effective method to control BrO_3^- is to inhibit its formation during the ozonation process (von Gunten, 2003b). This paper consolidates and critically reviews the published literature on EOPs. Based on the reviewed information, more work is required before some of these technologies can be put in practice, and the following suggestions for future studies can help move them toward commercialization:

1. The peroxone process is a well-understood technique and hence, there is almost no room for improvement for this technology. The presence of O_3, H_2O_2, and $^\bullet OH$ have different effects during the process of the e-peroxone process; therefore, it is important to methodically investigate the best-operating conditions for an e-peroxone process for different water characteristics. Moreover, it is important to verify that both the inhibition of BrO_3^- and oxidation of organics occur. The superiority of the PMS/O_3 system is the production of $SO_4^{\bullet-}$, a radical that is more powerful than $^\bullet OH$. The main disadvantage of the system as a control method for BrO_3^- is its infancy, with only one exisitng research study. Therefore, the system will require much more research on the BrO_3^- formation mechanism, as well as the effect of water matrices, before the technology can be put to use. Since carbon materials, such as reduced graphene oxide, showed promising results in inhibiting BrO_3^- formation during ozonation, future work can involve creating carbon-based and other cost-effective and environmentally friendly materials, with higher reduction and adsorption capacities, to control BrO_3^- formation during $SO_4^{\bullet-}$ based EOPs.

Table 6. Economic and technical characteristics of different enhanced ozonation processes for bromate control.

Techniques (full/pilot/bench-scale)	Cost-effective	Chemical cost and handling	Extra power required	Specific ratio needed	Automation	BrO_3^- formation reduced by organics	O_3 dose increases BrO_3^- formation	Regeneration	Catalyst Doping	If initial Br^- conc. increases, then	Phase
Peroxone (full scale)	No	Yes	No	Yes	No	Yes	Yes	N/A	N/A	BrO_3^-++	Liquid
Electro-peroxone (pilot scale)	Yes	No	Yes	No	Yes	Yes	Yes	N/A	N/A	BrO_3^-++	Liquid
Photolytic ozonation (pilot scale)	No	No	Yes	No	No	Yes	Yes	N/A	N/A	BrO_3^-++	Liquid/radiation
Mixed oxides (bench-scale)	Yes	Yes	No	Yes	No	Yes	Yes	No	No	BrO_3^-++	Solid
Mixed metal oxides (bench-scale)	Yes	Yes	No	Yes	No	No	Yes	No	No	BrO_3^-++	Solid
Ce-MCM (pilot scale)	Yes	Yes	No	Yes	No	NA	Yes	Yes	Yes	BrO_3^-++	Solid
Nano metal oxides (bench-scale)	Yes	Yes	No	No	No	Varies	No	No	No	BrO_3^-++	Solid
Layered double hydroxide (bench-scale)	NA	Yes	No	No	No	NA	No	No	No	NC	Solid
Iron oxide hydroxide (bench-scale)	NA	Yes	No	No	No	NA	No	No	No	NC	Solid
Manganese oxide (bench-scale)	NA	Yes	No	No	No	NA	No	No	No	NC	Solid
Sonozone (bench-scale)	No	No	Yes	No	Yes	NA	Yes	N/A	N/A	BrO_3^-++	Liquid/radiation

Note: NA is Not available, N/A Not applicable, variable means changes randomly, ++ means increases, NC is no change.

2. Photolytic ozonation was found to inhibit BrO_3^- formation, but its efficiency reduces in the presence of HA and/or NOM, which absorb UV radiation, thereby reducing the potential of this technique. Hence, there is a need to find ways to increase the efficiency of O_3/UV in the presence of NOM or HA. One suggestion is to increase the UV intensity or use a UV lamp emitting a wavelength below 200 nm. More research is needed to comprehend the detailed mechanisms of BrO_3^- mitigation by O_3-VUV. For example, the occurrence of bromine species during the O_3-VUV process and formation of H_2O_2 should be examined.

3. The addition of ferrate(VI) in water reduces BrO_3^- to a non-detectable concentration in the presence of phosphate. However, research is needed to investigate the role of phosphate in inhibiting BrO_3^- formation in the ferrate(VI)-O_3 system. Exploring the cost involved in using ferrate as a catalyst would be useful.

4. Layered double hydroxides and metal hydroxides reduced BrO_3^- formation almost completely, but the catalyst surface became saturated after a while as Fe^{2+} was converted to Fe^{3+}. Mn-MCM-41 reduced 96.7% BrO_3^- formation at pH 6.5, whereas Ce-MCM-48 removed BrO_3^- up to 91% with efficient micro-pollutant removal and was reusable as a catalyst, as opposed to non-reusable layered double hydroxides and metal hydroxides. Therefore, enhancing the regeneration or achieving a decrease in surface saturation of hydroxide catalysts is a topic worth investigating.

5. Suggested broad research topics for BrO_3^- mitigation include: the mechanisms of O_3 reaction with reduced metals; quantification of other ozonation by-products (e.g., epoxides, haloacetamides, multifunctional carbonyl-containing compounds, and peroxides) in the solution and at the catalyst surface; effects of solution pH, temperature, and radical scavengers on catalytic ozonation; leaching of metals from the catalyst; and identification of the catalyst service life.

6. Albeit sonozone was found to inhibit BrO_3^- formation under specific conditions, considering the limited amount of published literature, research on the effects of ozone CT and US power on the effectiveness of BrO_3^- reduction for water with different chemical characteristics (NOM, HA, and Br^- concentrations) is needed. Future studies should also identify the formation and effects of any sonozone by-products.

7. No mathematical models have been developed on BrO_3^- removal or formation inhibition using EOPs. Therefore, the modeling of BrO_3^- control by EOPs should be explored in future studies.

8. The technical and economic feasibility of a technology makes it viable for being employed in the industry. Table 6 briefly overviews the economic and technical characteristics of different enhanced ozonation

processes for BrO_3^- control. Additionally, Table 6 specifies the different scales (full, pilot or bench scale) at which the techniques have been explored so far. Based on the literature reviewed, most of the enhanced ozonation techniques (except peroxone) for the abatement of BrO_3^- formation have been achievable at bench scales; however, there is a dearth of comprehensive studies targeting the economic feasibility of the discussed techniques in a full-scale capacity.

9. Future research should evaluate the costs of BrO_3^- control by EOPs. The capital costs (reactor, piping, valves, site work, and contractor operations and procedures) and operating and maintenance costs (part replacement, labor, analytical work, chemical, and electrical) for each process should be evaluated with respect to water quality, flow rate, influent Br^- concentration, and required removal efficiency. These cost evaluations must be executable under similar conditions/constraints to allow a direct and fair comparison of different EOPs.

5. Conclusions

This paper reviews BrO_3^- formation mechanisms, along with inhibition and removal performances by enhanced ozonation techniques, in comparison with ozonation alone. Additionally, the paper highlights the advantages and disadvantages associated with each enhanced ozonation technique. Among the techniques reviewed and discussed, the peroxone process is the most explored technique with successful BrO_3^- control, whereas e-peroxone is an emerging process with the same performance. Catalytic ozonation is a promising technique to limit BrO_3^- formation. Ozonation with catalysts (akaganeite, layered double hydroxide, ferrate, and Ce-MCM) showed $> 91\%$ efficiency in BrO_3^- formation inhibition. However, only Ce-MCM can be regenerated. With the current information, sonozone emerges as the least efficient technique. Nano-metal oxides look promising for BrO_3^- reduction efficiencies but require further research since limited data were found on BrO_3^- mitigation by these catalysts.

It will be useful for water utilities to employ a technique that will reduce both BrO_3^- formation and carcinogenic risk (due to the formation of other DBPs) in treated water. Before implementing an enhanced ozonation technique, the utility must understand the limitations of the technique, including the level of both regulated (BrO_3^-) and unregulated (aldehydes, ketones, and carboxyl acids) DBPs that high O_3 dosages may produce. Considering these technologies, utilities employing ozonation must consider catalyst costs (synthesis, installation, maintenance, and replacement), energy consumption, personnel training requirements, and DBP identification before implementation.

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