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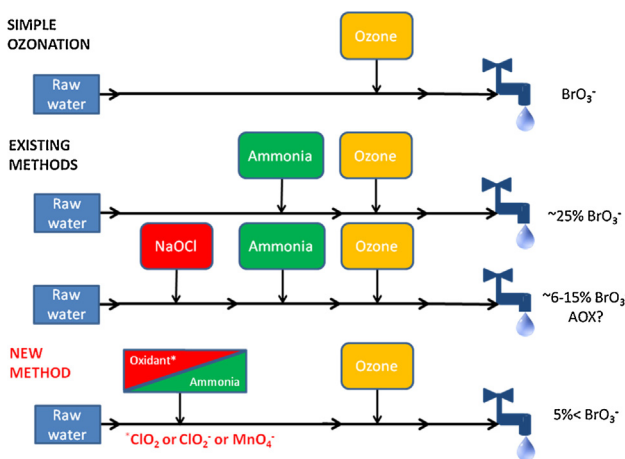
## Novel pre-treatments to control bromate formation during ozonation

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## HIGHLIGHTS

- Investigation of pre-treatments that inhibit bromate formation in ozonation.
- $\text{ClO}_2$  and  $\text{MnO}_4^-$  with  $\text{NH}_4^+$  were promising pre-treatments for bromate inhibition.
- Atrazine removal was only unaffected by the  $\text{MnO}_4^-$  with  $\text{NH}_4^+$  pretreatment.
- $\text{MnO}_4^-$  with  $\text{NH}_4^+$  pre-treatment appears technically and economically feasible.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Worldwide water shortage increase and water quality depletion from microbial and chemical compounds, pose significant challenges for today's water treatment industry. Both the development of new advanced oxidation technologies, but also the enhancement of existing conventional technologies is of high interest. This study tested improvements to conventional ozonation that reduce the formation of the oxidation-by-product bromate, while maintaining the effectiveness for removal emerging contaminants (atrazine).  $\text{MnO}_4^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_2$ ,  $\text{ClO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HSO}_5^-$  or  $\text{S}_2\text{O}_8^{2-}$  with  $\text{NH}_4^+$  were tested as pre-treatments to ozonation of ground water. Each oxidant and  $\text{NH}_4^+$  were added in a single stage or separately prior to ozonation. To the best of our knowledge, this is the first study that has tested all the above-mentioned oxidants for the same water matrix. Based on our results, the most promising pre-treatments were  $\text{MnO}_4^- - \text{NH}_4^+$ ,  $\text{ClO}_2^- - \text{NH}_4^+$  and  $\text{ClO}_2 - \text{NH}_4^+$ .  $\text{MnO}_4^- - \text{NH}_4^+$  was the only pre-treatment that did not inhibit atrazine removal. When compared with the previously proposed  $\text{Cl}_2/\text{NH}_4^+$  pre-treatment,  $\text{MnO}_4^- + \text{NH}_4^+$  was found as effective for preventing  $\text{BrO}_3^-$  formation, while atrazine removal was higher. In addition,  $\text{MnO}_4^- + \text{NH}_4^+$  can be added in a single stage (compared to the 2 stage addition of  $\text{Cl}_2/\text{NH}_4^+$ ) without causing the formation of potentially harmful chlorination-by-products.

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## 1. Introduction

The presence and subsequently the removal of emerging contaminants (ECs) like pesticides, hormones, medical drugs and naturally occurring toxic metabolites from water resources poses a challenge for the water industry [1–5]. In order to remove micropollutants in trace concentrations from water resources chemical oxidation technologies such as ozonation and advanced oxidation processes (AOPs) are increasingly applied in different types of source water [2,6–12]. Ozone ( $O_3$ ) is able to remove most ECs with less energy consumption than conventional UV/ $H_2O_2$  AOPs [12–14], but at higher capital costs and with a larger footprint of the treatment unit. The recently developed UV/ $Cl_2$  AOP appears to be a promising candidate for significantly reducing capital and operational costs for the oxidative removal of trace compounds especially from wastewater treatment plant effluents [15,16].

Nevertheless, ozonation remains a preferred method for the removal of organic ECs as it is a simple to control and implement at existing waterworks. In addition to water purification,  $O_3$  has been used for disinfection, taste, color, and odor removal, and the pre-oxidation of drinking water to reduce formation of byproducts in post treatment chlorination [17–19]. Ozone installations are currently found in many water treatment plants primarily for pathogen control and/or for taste and odor control such as the Metropolitan Water District of Southern California and Alameda County Water District in California [19]. This is because,  $O_3$  readily reacts with unsaturated bonds in organic molecules through *cyclo* addition reactions leading to the formation of unstable ozonides that eventually breakdown to aldehydes and ketones. Its ability to form hydroxyl radicals ( $HO^\bullet$ ) as a decomposition intermediate increases the oxidation efficiency of the technology by adding the possibility for non-selective oxidation [20]. A side effect of ozonation is the formation of bromate ( $BrO_3^-$ ) when the source water contains naturally occurring bromide ( $Br^-$ ) [17,21–23]. Bromate is a probable human carcinogen [22,24] and therefore its concentration is regulated in drinking water.  $BrO_3^-$  comprises the only ozonation by-product that is currently being regulated in drinking waters [18,25,26]. In the past, the drinking water standard limits for bromate have been decreased to 10.0  $\mu\text{g/L}$  in Europe and in the USA (0.010 mg/L) [25,26] even stronger restrictions (5  $\mu\text{g/L}$ ) have been considered for its annual average concentration [26–28]. Following extensive evaluation of the risks and benefits of ozonation the USEPA decided against the reduction of the  $BrO_3^-$  limit because technical analyses indicated that many facilities utilizing ozonation for improved disinfection would be unable to meet the stringent disinfection criteria under LT2ESWTR and maintain bromate formation below 0.005 mg/L, at the same time. This applies especially for facilities where chlorine-resistant microorganisms such as *Cryptosporidium* necessitate treatment [19,26,28,29].

The process in which  $BrO_3^-$  is formed during ozonation consists of two phases: a quick and a slow initiated by  $HO^\bullet$  and  $O_3$  respectively [30]. These mechanistic steps have been extensively studied and unveiled by von Gunten's research group and have been illustrated as a series of bimolecular reactions (Fig. 1) [8,30,31]. The 4 major steps that lead to  $BrO_3^-$  formation begin with  $O_3$  oxidizing bromide ( $Br^-$ ) to hypobromite ( $BrO^-$ ) or hypobromous acid ( $HBrO$ ), depending on the solution pH. Then,  $HBrO/OBr^-$  is oxidized by  $HO^\bullet$  to  $BrO^\bullet$ , followed by a disproportionation reaction ( $2BrO^\bullet \rightarrow BrO^- + BrO_2^-$ ) to give  $BrO_2^-$  and finally  $O_3$  oxidizes the latter ion to  $BrO_3^-$  [8]. A secondary pathway where  $HO^\bullet$  oxidizes bromide to its corresponding radical ( $Br^\bullet$ ), that either reacts with  $O_3$  or  $HO^\bullet$  to form  $BrO^\bullet$  or  $HOBr/BrO^-$ , respectively has also been reported. The oxidation of  $HBrO/BrO^-$  can also occur with  $O_3$  but at lower rates [8]. Identification of the mechanistic steps of  $BrO_3^-$  formation was crucial because it revealed its rate limiting steps and

consequently assisted in adopting practices that can significantly reduce  $BrO_3^-$  formation.

Based on this mechanistic understanding, several methods have been proposed to alter the water chemistry of the treated water in order to decrease the formation of bromate during the ozonation process. Depression of water pH to 6 shifts the equilibrium of  $HBrO/BrO^-$  towards  $HBrO$  which reacts slowly with  $O_3$  to form  $BrO_3^-$ , therefore  $BrO_3^-$  formation is hindered [31,32]. This pre-treatment has successfully and cost-effectively been applied in water facilities [19]. However if the treated water has moderate to high alkalinity (ground-water) the pH adjustment cost may be prohibitive reaching 2–9 times ozone's operational cost [27,28]. Another method is the  $Cl_2/NH_4^+$  pre-treatment [31].  $Cl_2$  is added prior to ozonation and oxidizes  $Br^-$  to  $HBrO/BrO^-$ , which then reacts with added  $NH_4^+$  to form bromamine ( $NH_2Br$ ,  $k_{NH_4^+/O_3} = 8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) [8,27,28,30,31]. Since the latter molecule is not significantly oxidized by  $O_3$  ( $k_{NH_2Br/O_3} = 40 \text{ M}^{-1} \text{ s}^{-1}$ ) [28],  $BrO_3^-$  formation is greatly reduced. However, this approach has some disadvantages including the formation of undesired chlorination by-products from the reaction of the added chlorine with organic matter and the need for sequential addition of  $Cl_2$  and  $NH_4^+$  since these chemicals readily react with each other to form chloramines. The most recently tested technology, is the coupling of photocatalysis to ozonation, which besides accelerating the degradation rates of ECs, it also limited bromate formation [33]. The effectiveness of these pre-treatments greatly depends on the quality of the treated water, including pH, NOM and alkalinity since they affect the oxidation routes followed and contact times of  $O_3$  or  $HO^\bullet$  [28,31,34].

In our earlier study, [34], the abovementioned pre-treatments were evaluated for their efficiency to inhibit bromate formation while achieving one log atrazine (herbicide) removal from  $Br^-$  spiked ground water from the DTU (Technical University of Denmark) Campus, which has high alkalinity ( $HCO_3^- = 332 \text{ mg/L}$ ,  $pH_0$  7.4) and a considerable concentration of 'aged' natural organic matter (NOM; DOC  $\sim 2.5 \text{ mg/L}$ ) [34]. This water presents an exceptional challenge for  $O_3$  treatment because both  $O_3$  and  $HO^\bullet$  are consumed by the NOM and high alkalinity, and consequently the required  $O_3$  dose for contaminant degradation is significantly increased along with  $BrO_3^-$  formation [35]. Our previous results indicated that a high  $O_3$  dose (3.5 mg/L) was needed to achieve 90% removal of atrazine from ground-water resulting in the formation of 130–170  $\mu\text{g/L}$   $BrO_3^-$ . The  $O_3$ -dose required to remove atrazine was unaffected even when ozone was applied as peroxide ( $O_3/H_2O_2$  1:3.5 w/w), though it limited  $BrO_3^-$  formation below the drinking water limit of 10  $\mu\text{g/L}$ . Depression of pH to 6 was proven insufficient to control  $BrO_3^-$  formation below the 10  $\mu\text{g/L}$  limit in the ground water from the DTU Campus. Pretreatment with  $Cl_2/NH_4^+$  reduced  $BrO_3^-$  formation close to the 10  $\mu\text{g/L}$  limit; however, atrazine removal was reduced to below 75%.

Based on the above, this co-operative study between Siemens Water Technologies and DTU aimed to investigate the efficiency of several oxidants commonly used in water treatment as replacements of  $Cl_2$  in the " $Cl_2/NH_4^+$ " pre-treatment for inhibiting  $BrO_3^-$  formation during ozonation to exceed the limit of 10  $\mu\text{g/L}$ . It was anticipated that these alternatives may be advantageous to  $Cl_2$ , since they do not form chlororganic byproducts nor react directly with  $NH_4^+$ . Therefore, sodium hypochlorite ( $NaClO$ ) [22,36] and chlorine dioxide ( $ClO_2$ ) [21,32], and the never before tested paracetic acid ( $CH_3COOOH$ , PAA), potassium persulfate ( $K_2S_2O_8$ ), peroxymonosulfate ( $KHSO_5$ ), and potassium permanganate ( $KMnO_4$ ) were used in this study. Apart from monitoring  $BrO_3^-$  formation for each pre-treatment, the effect of the concentration of the oxidant and  $NH_4^+$  added were investigated. Also, the extent to which these pre-treatment affected atrazine removal during ozonation, was monitored. Atrazine was chosen as the model EC

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