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Reduction of Bromate Formation During Ozonation of Drinking Water

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Summary

This study focused on the prevention of carcinogenic bromate formation during ozonation of tap water from the DTU university campus. To achieve this, different pre-treatments including pH-adjustment, ammonia addition and chlorine-ammonia addition, were tested. Formation of bromated was drastically reduced by each pretreatment while the required ozone dose for 90% atrazine removal increased at different degree for each pre-treatment.

Keywords

Ozonation, ammonia process, ammonia-chlorine process, advanced water treatment

Introduction

Modern living especially in developed economies has led to the abundant use of pharmaceuticals, personal care products (PCPs), hormones, pesticides, and other environmentally persistent chemicals, commonly known as micropollutants. Many of these after their use, find their way to water bodies as well as to drinking water resources (Koplin et al, 2003). The major concern for their presence in water is that their effect on human and animal health after long term exposure is unknown. In addition, they are non- biodegradable and only partly removed after treatment. For their successful removal, oxidation technologies like ozonation (O_3) and Advanced Oxidation Processes (AOPs) are utilized in an increasing number of facilities each year. The main drawback of contaminant degradation by O_3 or O_3 based AOPs, such as O_3/H_2O_2 and O_3/UV is the formation of the carcinogenic bromate (BrO_3^-) from bromide (Br^-). This reaction occurs via O_3 oxidation pathway and not via $HO^•$ radical pathway (Pinkernell and von Gunten, 2001, von Gunten 2003). The stringent bromate limits (10µg/L) have became prohibitive for the application of many O_3 based processes for drinking water treatment, even though they are known to be efficiently degrading recalcitrant contaminants while being relatively cost-effective treatments. Therefore, this study focused on finding ways to reduce bromate formation during ozonation, by utilizing different pre-treatments.

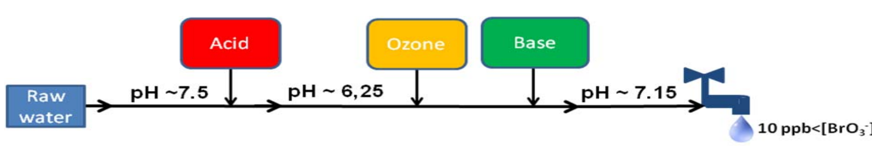
Materials and Methods

The treated solutions were prepared in DTU tap water which were first adjusted at pH values equal to 6, and 7 and then spiked with 200 µg/L of atrazine and 100 µg/L of Br^-. Ammonia and sodium hypochlorine was spiked into the water from 1 g/L stock solutions. All the pretreatments and ozonation were performed at T = 15 °C.

Results and Discussion

Pretreatment with pH-reduction prior ozonation

The most commonly used pre-treatment prior ozonation to prevent bromate formation is pH adjustment to pH = 6.0 (Scheme 1). This process modification is somewhat expensive in chemical cost since base needs to be added to the water to return the pH to above 7 in order to prevent corrosion of pipes.



Scheme 1 Treatment chain for water acidification pre-treatment prior to ozonation.

Ozonation experiments at pH values 6 and 7 were performed to determine bromate formation during contaminant degradation. The ozone dose was set at 3.5 mg/L, the required dose to achieve the treatment goal of 90% atrazine removal. For pH = 6 two different batches A and B were tested and one for pH = 7. At neutral pH, ozonation with 3.5 mg/L results in the formation of 160 µg/L of BrO_3^- while at pH = 6, the average BrO_3^- concentration is ~ 90µg/L and atrazine were below the treatment target in both pH values (**Figure 1**). Reduction of pH to 6 resulted in 45% reduction of BrO_3^- formation; however a significant amount BrO_3^- was still generated (9 times higher than the 10 µg/L BrO_3^- provisional limit). This means that depending on the water source, the reduction of pH is not always a reliable tool to control bromate formation and alternative approaches should be followed.

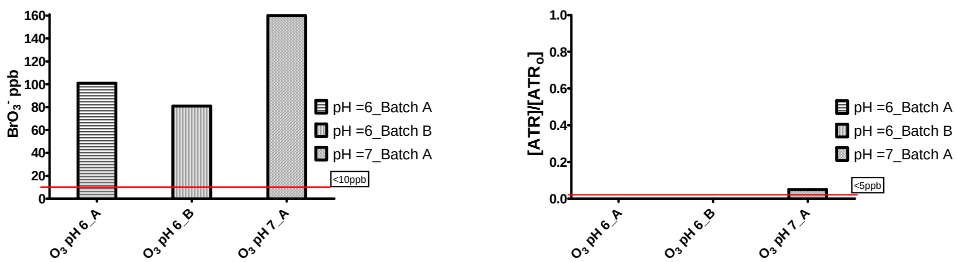


Figure 1 left: Bromate formation at different pH values at O3=3.5 ppm; **right:** Remaining atrazine at different pH values at O_3=3.5 ppm.

Ammonia and ammonia-chlorine pre-treatments

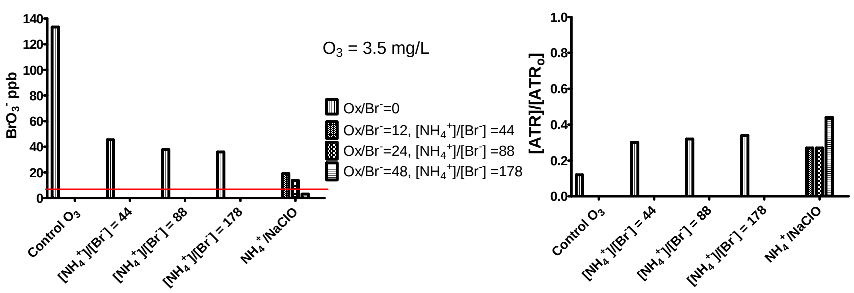


Figure 1: Effect of pre-treatment type and dosing on BrO_3^- formation **(left)** and ATR **(right)** removal during ozonation

Figure 1 (left), summarizes the results from the different pre-treatments on the bromated formation. The addition of ammonia (which reacts with hypobromite and forms bromamines instead of bromate), resulted in a decrease of bromate concentration of ~60% compare to the ozone control, irrespective of the ammonia dosing, meaning that lower concentrations than 1 mg/L ammonia ($[NH_4^+]/[Br^-]$ = 44) could be used. Pre-treatments with chlorine (as OCl^-), and ammonia, also reduced the formation of bromate. With increasing oxidant and ammonia concentrations, bromate formation reduced from 20 µg/L to below detection limit (BDL). As far as atrazine removal, ozonation alone efficiently removes atrazine at 90% target removal (Figure 1, right). At the same time, the presence of ammonia reduces the efficiency to 60% -65%. Chlorine was the least effective for atrazine removal with the efficiency being around 40-65%. A general trend is observed where the more efficient a pre-treatment is to reduced bromate formation, the lower atrazine removal is.

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