Water Research 130 (2018) 322–332

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Effects of conventional ozonation and electro-peroxone pretreatment of surface water on disinfection by-product formation during subsequent chlorination

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ARTICLE INFO

Article history:
Received 9 August 2017
Received in revised form
4 December 2017
Accepted 10 December 2017
Available online 11 December 2017

Keywords:
Bromate
Chlorination
Disinfection by-products
Electrochemical advanced oxidation process
HAAs
THMs

ABSTRACT

The electro-peroxone (E-peroxone) process is an emerging ozone-based electrochemical advanced oxidation process that combines conventional ozonation with *in-situ* cathodic hydrogen peroxide (H_2O_2) production for oxidative water treatment. In this study, the effects of the E-peroxone pretreatment on disinfection by-product (DBP) formation from chlorination of a synthetic surface water were investigated and compared to conventional ozonation. Results show that due to the enhanced transformation of ozone (O_3) to hydroxyl radicals (•OH) by electro-generated H_2O_2, the E-peroxone process considerably enhanced dissolved organic carbon (DOC) abatement and significantly reduced bromate (BrO_3^-) formation compared to conventional ozonation. However, natural organic matter (NOM) with high UV_{254} absorbance, which is the major precursors of chlorination DBPs, was less efficiently abated during the E-peroxone process than conventional ozonation. Consequently, while both conventional ozonation and the E-peroxone process substantially reduced the formation of DBPs (trihalomethanes and haloacetic acids) during post-chlorination, higher DBP concentrations were generally observed during chlorination of the E-peroxone pretreated waters than conventional ozonation treated. In addition, because of conventional ozonation or the E-peroxone treatment, DBPs formed during post-chlorination shifted to more brominated species. The overall yields of brominated DBPs exhibited strong correlations with the bromide concentrations in water. Therefore, while the E-peroxone process can effectively suppress bromide transformation to bromate, it may lead to higher formation of brominated DBPs during post-chlorination compared to conventional ozonation. These results suggest that the E-peroxone process can lead to different DBP formation and speciation during water treatment trains compared to conventional ozonation.

1. Introduction

Chlorine has been used as a disinfectant in water treatment for more than 100 years. Chlorine can inactivate a wide range of waterborne pathogens (bacteria and viruses) and maintain a residual disinfectant in treated-water distribution systems (Crittenden et al., 2012). Because of its low cost and easy accessibility, chlorine is still the most used disinfectant in drinking water treatment globally (Rosario-Ortiz et al., 2016). However, chlorine can react with natural organic matter (NOM) present in source waters to form harmful halogenated disinfection by-products (DBPs) (Gallard and von Gunten, 2002; Hrudey and Charrois, 2012; Reckhow et al., 1990; Richardson, 2011; Sedlak and von Gunten, 2011). Among the known specific chlorination DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) are the two most prevalent groups and regulated in many countries (USEPA,

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https://doi.org/10.1016/j.watres.2017.12.019

1998; WHO, 2011).

One option to reduce the DBP formation during chlorination is to pretreat source waters with ozone (O_3). Many studies have shown that ozonation can destruct a considerable fraction of DBP precursors in natural water, and therefore reduce the DBP formation during subsequent chlorination (Chang et al., 2002; de Vera et al., 2016; Gallard and von Gunten, 2002; Hua and Reckhow, 2007; 2013; Mao et al., 2014). In addition, O_3 can effectively inactivate some chlorine-resistant protozoa (e.g., *Cryptosporidium parvum* oocysts), and oxidize many inorganic and organic contaminants (e.g., iron, manganese, pesticides, and pharmaceuticals) that may be present in drinking water sources (von Gunten, 2003a; von Sonntag and von Gunten, 2012). However, O_3 decays rapidly in water, and therefore is unable to provide long-lasting secondary disinfection in distribution systems (Crittenden et al., 2012; Rosario-Ortiz et al., 2016). Therefore, post-chlorination is still needed to maintain a disinfection residual in most drinking water distribution systems. Moreover, ozonation of bromide-containing water can lead to the formation of bromate (BrO_3^-) (von Gunten, 2003b; von Gunten and Oliveras, 1998), which is an oxidation/disinfection by-product with a low drinking water standard of 10 μg/L in many countries (USEPA, 1998; WHO, 2011).

To reduce bromate formation, we have tested combining conventional ozonation with *in-situ* electrochemical generation of hydrogen peroxide (H_2O_2) from cathodic oxygen (O_2) reduction (Li et al., 2015; Yao et al., 2017). The electro-generated H_2O_2 can accelerate O_3 transformation to hydroxyl radicals (•OH), thus lowering the residual concentrations of O_3, which is an indispensable reactant in the •OH-induced bromate formation mechanism (von Gunten, 2003b; von Gunten and Oliveras, 1998; von Sonntag and von Gunten, 2012). In addition, H_2O_2 can rapidly reduce hypobromous acid (HOBr, a key intermediate for bromate formation in O_3-induced processes) back to bromide (Br^-), thus impeding the formation pathways of bromate (von Gunten and Oliveras, 1997). Consequently, significantly less bromate is formed during the combined ozonation and electrochemical process (called as the electro-peroxone (E-peroxone) process (Yuan et al., 2013)) than during conventional ozonation (Li et al., 2015; Yao et al., 2017). Furthermore, due to the enhanced transformation of O_3 to •OH, the abatement of ozone-resistant contaminants (e.g., methylisoborneol and geosmin) can be improved in the E-peroxone process (Lin et al., 2016; Yao et al., 2017).

While the E-peroxone process can effectively inhibit bromate formation during the treatment of bromide-containing water (Li et al., 2015; Yao et al., 2017), its effects on the DBP formation during subsequent chlorination are still not known. The electro-generation of H_2O_2 and its enhancement of O_3 transformation to •OH shift the mechanisms of NOM oxidation from mainly selective oxidation with O_3 in conventional ozonation to less selective oxidation with •OH in the E-peroxone process (Li et al., 2015). Unlike O_3, which reacts preferentially with organics having conjugated double bonds and activated aromatic systems, •OH is a less selective oxidant and tends to react fast with almost all types of organics (Hammes et al., 2006; von Gunten, 2003a; Wert et al., 2007). The different mechanisms of the reactions of NOM with O_3 and •OH can have complex and distinct impacts on DBP formation during post-chlorination (de Vera et al., 2016; De Vera et al., 2015; Kleiser and Frimmel, 2000). In fact, contradictory results have been reported when comparing DBP formation during chlorination of waters pretreated by conventional ozonation and the conventional peroxone (O_3/H_2O_2) process. In some studies, conventional peroxone process results in higher THM formation during post-chlorination than for conventional ozonation (de Vera et al., 2016; De Vera et al., 2015; Irabelli et al., 2008; Mosteo et al., 2009; Wang et al., 2013). In contrast, others reported that THM formation was generally comparable (within experimental errors) for waters pretreated by the two processes, while HAA formation could either increase or decrease when conventional ozonation was changed to the conventional peroxone process (Lamsal et al., 2011; Yang et al., 2012). These results suggest that the E-peroxone process may result in different DBP formation during water treatment trains compared to conventional ozonation, which has yet to be evaluated.

Therefore, the main objective of this study was to investigate the effects of the E-peroxone pretreatment on DBP formation during post-chlorination. Synthetic surface waters were prepared according to typical drinking water quality in China, and then treated by consecutive conventional ozonation and chlorination (O_3-Cl_2) or consecutive E-peroxone and chlorination (EP-Cl_2) processes. The formation of DBPs (bromate, THMs, and HAAs) during the two consecutive processes were compared. The effects of key operational parameters of the E-peroxone process (O_3 doses and applied currents) on DBP formation were evaluated systematically.

2. Materials and methods

2.1. Synthetic surface water samples and reagents

Synthetic surface water was prepared by adding appropriate amounts of $CaCl_2$, $MgSO_4$, $NaHCO_3$, KBr (analytical grade), and humic acid stock solution to deionized water (see Table 1 for the main water quality parameters). This composition was intended to simulate typical drinking water quality in China (Wang et al., 2013), and similar effects have been observed for the E-peroxone process (e.g., reduced bromate formation and enhanced DOM mineralization) in the synthetic water and in a real surface water (Li et al., 2015). The humic acid stock solution was prepared by dissolving 250 mg humic acid (Sigma-Aldrich) in 100 mL deionized water at pH 12, followed by filtration through 0.45 μm Durapore membrane filters (Merck, Ireland). The stock solution was then stored in the dark at 4 °C before it was used to prepare the synthetic water. In addition, to investigate the role of bromide for the formation of bromate and brominated DBPs during ozonation and chlorination, the synthetic water was spiked to achieve an initial bromide concentration of 150 μg/L.

All DBP standards (e.g., trichloromethane, trichloroacetic acid, and dichloroacetic acid) were purchased from Sigma-Aldrich. The other reagents (e.g., $CaCl_2$, $MgSO_4$, and KBr) were of analytical grade and purchased from Modern Eastern Fine Chemical (Beijing, China). All solutions were prepared with deionized water.

Table 1
Main water quality parameters of the synthetic water used in this study.

Parameters	Value
DOC (mg C/L)	3.2
UV_{254} (cm^{-1})	0.25
Br^- (μg/L)	150
pH	8.0
Alkalinity (mg/L as $CaCO_3$)	75
Conductivity (μS/cm)	417
Ca^{2+} (mg/L)	29
Mg^{2+} (mg/L)	10
Na^+ (mg/L)	35
HCO_3^- (mg/L)	90
Cl^- (mg/L)	51
SO_4^{2-} (mg/L)	41