



# Formation of halogenated disinfection by-products in cobalt-catalyzed peroxymonosulfate oxidation processes in the presence of halides



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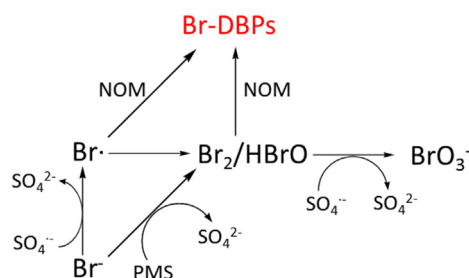
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## HIGHLIGHTS

- Br<sup>-</sup> can be transformed to reactive bromine species by both SO<sub>4</sub><sup>-</sup> and PMS.
- Reactive bromine species can react with NOM to form Br-DBPs.
- Br-DBPs can be further degraded by SO<sub>4</sub><sup>-</sup> but not PMS.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Sulfate radicals (SO<sub>4</sub><sup>-</sup>) generated by activation of peroxymonosulfate (PMS) and persulfate (PS) are highly oxidative and applied to degrade various organic pollutants. This research was designed to investigate formation of halogenated by-products in Co<sup>2+</sup> activated PMS process in the presence of halides and natural organic matter (NOM). It was revealed that no halogenated by-products were detected in the presence of Cl<sup>-</sup> while 189 μg/L bromoform and 100.7 μg/L dibromoacetic acid (DBAA) were found after 120 h when 2 mg/L NOM, 0.1 mM Br<sup>-</sup>, 1.0 mM PMS, and 5 μL Co<sup>2+</sup> were present initially. These products are known as disinfection by-products (DBPs) since they are formed in water disinfection processes. Formation of DBPs was even more significant in the absence of Co<sup>2+</sup>. The data indicate that both PMS and SO<sub>4</sub><sup>-</sup> can transform Br<sup>-</sup> to reactive bromine species which react with NOM to form halogenated by-products. Less DBP formation in Co<sup>2+</sup>-PMS systems was due to the further destruction of DBPs by SO<sub>4</sub><sup>-</sup>. More DBPs species including chlorinated ones were detected in the presence of both Cl<sup>-</sup> and Br<sup>-</sup>. However, more brominated species produced than chlorinated ones generally. The total DBP yield decreased with the increase of Cl<sup>-</sup> content when total halides kept constant. This is one of the few studies that demonstrate the formation of halogenated DBPs in Co<sup>2+</sup>/PMS reaction systems, which should be taken into consideration in the application of SO<sub>4</sub><sup>-</sup> based oxidation technologies.

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## 1. Introduction

Advanced oxidation processes (AOPs) are important technologies for organic pollution control. AOPs usually generate highly reactive radicals which are responsible for the degradation of

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contaminants. Hydroxyl radical ( $\text{OH}^\bullet$ ,  $E^0 = 1.9\text{--}2.7$  V) and sulfate radicals ( $\text{SO}_4^\bullet$ ,  $E^0 = 2.5\text{--}3.1$  V) (Neta et al., 1988; Anipsitakis and Dionysiou, 2003) are the commonly used radical species in AOPs. The well-known Fenton and Fenton-like oxidation processes rely primarily on  $\text{OH}^\bullet$  generated by iron catalyzed decomposition of  $\text{H}_2\text{O}_2$ . Recently,  $\text{SO}_4^\bullet$  based AOPs attracted considerable attention to the research community. Sulfate radical can be produced by activation of persulfate (PS) (Johnson et al., 2008; Liang and Bruell, 2008; Furman et al., 2010; Adewuyi and Sakyi, 2013; Al-Shamsi and Thomson, 2013; Hazime et al., 2014) or peroxymonosulfate (PMS) (Anipsitakis and Dionysiou, 2003; Costanza et al., 2010; Yao et al., 2012) by heat, UV light, transient metals, or UV/TiO<sub>2</sub>. Sulfate radical has a comparable redox potential to  $\text{OH}^\bullet$ . More importantly, it has a wider operational pH range than  $\text{OH}^\bullet$  because the latter can only maintain high oxidation potential at acidic conditions (Anipsitakis and Dionysiou, 2003; Guan et al., 2011). In addition to the oxidation strength, the precursors of  $\text{SO}_4^\bullet$  (PMS and PS) are more stable and easier to handle than those of  $\text{OH}^\bullet$  ( $\text{H}_2\text{O}_2$  and  $\text{O}_3$ ), which enables them more readily delivered to sub-surface (Liang et al., 2007, 2008). Due to these advantages,  $\text{SO}_4^\bullet$  based AOPs can serve as *in situ* remediation technologies to address contaminated soils and groundwaters.

Owing to the high oxidation potential,  $\text{SO}_4^\bullet$  also reacts with various non-targeted constituents in the environmental matrix. Attention has been paid to the transformation of halides and formation of halogenated by-products in  $\text{SO}_4^\bullet$  based oxidation processes (Fang and Shang, 2012; Wang et al., 2014; Lu et al., 2015). It was demonstrated that  $\text{Br}^-$  could be oxidized to form bromate ( $\text{BrO}_3^-$ ) as the final product in UV/PS and  $\text{Co}^{2+}$ /PMS processes, during which hypobromous acid ( $\text{HBrO}$ ) was a key intermediate (Fang and Shang, 2012; Lutze et al., 2014). Chloride was found to follow a similar transformation scheme in UV/PS process at acidic condition (Lutze et al., 2015). During the transformation of halides in  $\text{SO}_4^\bullet$  based AOPs, a series of reactive halogen intermediate species such as halogen atom ( $\text{X}^\bullet$ ), halogen radical ( $\text{X}_2^\bullet$ ), and free halogen ( $\text{X}_2$ ,  $\text{HXO}$ ) can be generated (Lutze et al., 2014; Yang et al., 2014; Li et al., 2015; Liu et al., 2015; Lutze et al., 2015). These halogen species can potentially react with natural organic matter (NOM) or other organic compounds resulting in the formation of organic halogen. For example, bromoform and bromoacetic acids were found in heat activated PS oxidation and heterogeneous catalytic activation of PMS processes in the presence of NOM and  $\text{Br}^-$  (Wang et al., 2014; Lu et al., 2015). The halogenation of NOM is analogous to that occurs during water chlorination processes. Phenolic moieties in NOM molecules are believed to be the primary sites responsible for halogen attack leading to the formation of a variety of halogenated by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Lu et al., 2004; Zhai and Zhang, 2011; Pan and Zhang, 2013). This process may involve a series of reactions including substitution, oxidation, and hydrolysis. Formation of halogenated aromatic intermediates which could further decomposed to form THMs and HAAs has been demonstrated using MS technology (Zhai and Zhang, 2011; Pan and Zhang, 2013).

THMs and HAAs are known as disinfection by-products (DBPs) because they are formed in drinking water disinfection processes. Bromate is also a regulated DBP formed in ozone disinfection process. DBPs are verified to be associated with notable health risks and cause global concern (Xie, 2003; Dad et al., 2013; Yang and Zhang, 2013). Halides are ubiquitously presented in natural environment. Bromide concentrations range from a few to hundreds of  $\mu\text{g/L}$  in fresh waters, depending primarily on local geochemistry conditions. Anthropogenic sources of bromide are usually insignificant. (Magazinovic et al., 2004). Chloride in natural waters has both natural and anthropogenic sources, such as seawater intrusion

in coastal areas, run-off containing road de-icing salts, the use of inorganic fertilizers, septic tank effluents, etc. Background concentrations of  $\text{Cl}^-$  are on the order of 1–100 mg/L in fresh waters (WHO, 1996). Thus, formation of halogenated DBPs is possible when  $\text{SO}_4^\bullet$  is applied to treat contaminated soils and groundwaters. Nonetheless, this problem is largely overlooked. Many halogenated DBPs are persistent chemicals. The lifetimes of haloacetic acids can be decades in natural waters (Lifongo et al., 2010). Thus, potential formation of DBPs and associated risks to the ecosystems and human beings in  $\text{SO}_4^\bullet$  based oxidation processes warrant careful consideration. In the present study, transformation of bromide in  $\text{Co}^{2+}$ /PMS oxidation process was explored. Although previous studies have revealed that  $\text{Br}^-$  could be converted to  $\text{BrO}_3^-$  in this process (Li et al., 2015), little attention was paid to the formation of organic brominated by-products. In addition, potential formation of chlorinated by-products in the presence of  $\text{Cl}^-$  remains unexplored. Findings of this work are of relevance to evaluate the feasibility of  $\text{Co}^{2+}$ /PMS oxidation process in real treatment practice for contaminated sites and help to optimize this process.

## 2. Material and methods

### 2.1. Materials

All chemicals were of reagent grade or better.  $\text{KHSO}_5$ ,  $\text{CoSO}_4$ ,  $\text{KBr}$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_3$ , and *N,N*-dimethyl-1,4-phenylenediamine monohydrochloride (DPD) were purchased from Aladdin (Shanghai, China). *tert*-Butyl methyl ether (MTBE) was HPLC grade and obtained from Fisher (Waltham, MA). Trihalomethanes (THMs) and haloacetic acids (HAAs) calibration standards were purchased from Sigma-Aldrich (St. Louis, MO). NOM stock solution was prepared by reconstitute Suwannee River natural organic matter obtained from the International Humic Substances Society (IHSS). Total organic carbon (TOC) of the NOM solutions was determined using a Shimadzu 5050A TOC analyzer.

### 2.2. Batch reactions

Formation of DBPs was explored in a series of glass vials (42 mL) as batch reactors at 20 °C. The reactors were filled with synthetic water samples prepared by dissolving 0.1 mM halides, 2.0 mg/L (as TOC) NOM, and 10 mM phosphate buffer (pH 6.5) in ultra pure water. The halides consisted of  $\text{Cl}^-$  and  $\text{Br}^-$  with total concentration of 0.1 mM but  $\text{Cl}^-/\text{Br}^-$  molar ratios varied. The reaction was initiated by adding 5  $\mu\text{M}$   $\text{Co}^{2+}$  and certain amount (1 and 5 mM) of PMS sequentially. At preset reaction time during a time course of 120 h, 2 vials were quenched by adding 1 mM  $\text{Na}_2\text{SO}_3$  and kept in the refrigerator until further treatment and analysis for THMs and HAAs. No headspace was left in the vials during the entire reaction and storage period. Control experiments with  $\text{Co}^{2+}$  absent were conducted concurrently.

### 2.3. Analysis of THMs and HAAs

THMs were analyzed by liquid-liquid extraction according to EPA method 551.1 using an Agilent 7890 gas chromatograph (GC) equipped with an electron capture detector (ECD) and a DB5- fused silica capillary column (30 m  $\times$  0.53 mm  $\times$  1.5  $\mu\text{m}$ ). After a 30 mL sample aliquot was extracted with 3 mL MTBE and analyzed with GC. The temperature program used to separate the analytes was as follows: initial temperature of 35 °C held for 12 min, then increased at a rate of 8 °C/min to 190 °C, held for an additional 3 min. The temperature of the injector and detector were 200 and 350 °C, respectively. Five aqueous calibration standards, bracketing the analyte concentration range expected in the samples, were

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