

# Formation of brominated disinfection by-products and bromate in cobalt catalyzed peroxymonosulfate oxidation of phenol



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## ARTICLE INFO

### Article history:

Received 23 April 2015

Received in revised form

6 July 2015

Accepted 8 July 2015

Available online 14 July 2015

### Keywords:

Sulfate radical

Phenol

Brominated disinfection by-products

Bromate

Reaction pathway

## ABSTRACT

Formation of halogenated disinfection by-products (DBPs) in sulfate radical ( $\text{SO}_4^{\cdot-}$ ) based oxidation processes attracted considerable attention recently. However, the underlying reaction pathways have not been well explored. This study focused on the transformation of  $\text{Br}^-$  in cobalt activated peroxymonosulfate ( $\text{Co}^{2+}/\text{PMS}$ ) oxidation process. Phenol was added as a model compound to mimic the reactivity of natural organic matter (NOM). It was revealed that  $\text{Br}^-$  was efficiently transformed to reactive bromine species (RBS) including free bromine and bromine radicals ( $\text{Br}^\cdot$ ,  $\text{Br}_2^{\cdot-}$ , etc.) in  $\text{Co}^{2+}/\text{PMS}$  system.  $\text{SO}_4^{\cdot-}$  played a principal role during this process. RBS thus generated resulted in the bromination of phenol and formation brominated DBPs (Br-DBPs) including bromoform and bromoacetic acids, during which brominated phenols were detected as the intermediates. Br-DBPs were further degraded by excessive  $\text{SO}_4^{\cdot-}$  and transformed to bromate ultimately. Free bromine was also formed in the absence of  $\text{Co}^{2+}$ , suggesting  $\text{Br}^-$  could be oxidized by PMS *per se*. Free bromine was incorporated to phenol sequentially leading to Br-DBPs as well. However, Br-DBPs could not be further transformed in the absence of  $\text{SO}_4^{\cdot-}$ . This is the first study that elucidated the comprehensive transformation map of  $\text{Br}^-$  in PMS oxidation systems, which should be taken into consideration when PMS was applied to eliminate contamination in real practice.

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## 1. Introduction

Sulfate radical ( $\text{SO}_4^{\cdot-}$ ) having a redox potential of 2.5–3.1 V (Fang and Shang, 2012; Furman et al., 2010; Liang et al., 2008) is a strong oxidant comparable with hydroxyl radical ( $\text{HO}^\cdot$ ) (2.4–2.7 V) at acidic pH. It reacts with various organic and inorganic compounds at second-order rate constants ranging from  $10^6$  to  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Neta et al., 1977).  $\text{SO}_4^{\cdot-}$  can be generated by activation of persulfate (PS) (Adewuyi and Sakyi, 2013; Costanza et al., 2010;

Liang and Bruell, 2008) and peroxymonosulfate (PMS) (Anipsitakis and Dionysiou, 2003) via UV light, heat, chelated or unchelated transition metals,  $\text{H}_2\text{O}_2$ , and base (Anipsitakis and Dionysiou, 2003; Anipsitakis et al., 2005; Gilbert and Stell, 1990; Gilbert et al., 1988). Unlike the precursors of  $\text{OH}^\cdot$  (ozone and hydrogen peroxide), PS and PMS are highly soluble and stable (Guan et al., 2011), which offers great advantages in treating contaminants in subsurface. Thus, as an *in-situ* chemical oxidation (ISCO) technology (Sharma et al., 2000),  $\text{SO}_4^{\cdot-}$  based advanced oxidation process (SR-AOPs) has attracted increasing attention in soil and groundwater remediation (Bandala et al., 2008; Ikehata and El-Din, 2004; Long et al., 2014).

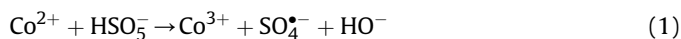
Of various activation methods, transition metal mediated activation attracts particular attention due to its cost-effectiveness and high efficiency. PMS, which is a component of a triple salt with the formula  $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ , is widely used as an oxidant instead of chlorine in the paper and pulp industry as well as cleaning agent in pools and spas disinfection (Zheng and Richardson, 1995). Previous studies have verified the well performance of cobalt catalyzed PMS ( $\text{Co}^{2+}/\text{PMS}$ ) oxidation of organic pollutants in aqueous solutions (Chan and Chu, 2009; Rivas et al., 2012; Yang et al., 2008). It is well accepted that  $\text{Co}^{2+}$  was the best

*Abbreviations:* DBPs, disinfection by-products; PMS, peroxymonosulfate; NOM, natural organic matter; RBS, reactive bromine species; Br-DBPs, brominated DBPs; PS, persulfate; ISCO, *in-situ* chemical oxidation; SR-AOPs, based advanced oxidation process; TOC, total organic carbon; DPD, N,N-dimethyl-1,4-phenylenediamine monohydrochloride; MTBE, methyl *tert*-butyl ether; THMs, trihalomethanes; HAAs, haloacetic acids; HPLC, high performance liquid chromatography; ESI, electron-spray ionization; MS, mass spectrum; MW, molecular weight; GC, gas chromatograph; ECD, electron capture detector; ICP, inductively coupled plasma; HPLC/MS, high performance liquid chromatography/mass spectrometry; DBAA, dibromoacetic acid; TBAA, tribromoacetic acid; MBAA, monobromoacetic acid; TIBr, total inorganic bromine.

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catalyst for PMS activation to generate  $\text{SO}_4^{\cdot-}$  (Anipsitakis and Dionysiou, 2004), and freely diffusible  $\text{SO}_4^{\cdot-}$  is the primary oxidizing species responsible for contaminants' degradation (Eqs. (1) and (2)).



Halides are ubiquitously present in natural environment. They can be transformed by  $\text{SO}_4^{\cdot-}$  to reactive halogen species such as  $\text{X}^{\cdot}$ ,  $\text{X}_2^{\cdot-}$ ,  $\text{XOH}^{\cdot-}$ ,  $\text{X}_2$ , and  $\text{XOH}$  (Yang et al., 2014). These reactive halogen species are moderate oxidants and can attack electron-rich compounds producing halogenated products. For instance, chlorinated phenols could be formed in SR-AOPs in the presence of phenols and  $\text{Cl}^-$ . Alken found that the presence of chloride strongly interfered the total organic carbon (TOC) analysis of seawater samples in  $\text{SO}_4^{\cdot-}$  based TOC analyzer due to the formation of chlorinated products such as chloromethane, chloroform, and methylene chloride (Alken, 1992). Bromide ( $\text{Br}^-$ ) is theoretically more readily oxidized upon contacting  $\text{SO}_4^{\cdot-}$ . It was demonstrated that  $\text{Br}^-$  could be converted to carcinogenic bromate ( $\text{BrO}_3^-$ ) in UV activated PMS oxidation process (Fang and Shang, 2012). More recently, Wang et al. (2014) reported the formation of bromoform and bromoacetic acids in  $\text{CuFe}_2\text{O}_4$  activated PMS oxidation process in the presence of  $\text{Br}^-$  and natural organic matter (NOM). Both  $\text{BrO}_3^-$  and the brominated organics are known as disinfection by-products (DBPs) which are usually formed in water disinfection processes and cause global concern due to their hazardous effects to human health (Jeong et al., 2011; Karanfil et al., 2008; World Health Organization, 2011).

It is widely accepted that free halogen attacks the phenolic moieties in NOM molecules leading to the formation of halogenated DBPs in water chlorination. However, little is known with regard to how halogens were transformed and incorporated into organic molecules in  $\text{SO}_4^{\cdot-}$  based oxidation processes, which comprises the main purpose of this study. Due to the uncertainty of NOM structures, phenolic compounds with well-defined molecular structures were often used to mimic their reactivity in the study of DBP formation (Ahmad et al., 2013). Such an approach was adopted in the present work. Phenol was selected as a NOM model compound in an attempt to elucidate the mechanisms and reaction pathways involved in the bromination processes during  $\text{Co}^{2+}$ /PMS oxidation. To the best of our knowledge, this is the first publication that reports a comprehensive transformation map of  $\text{Br}^-$  in PMS oxidation process.

## 2. Materials and methods

### 2.1. Reagents and materials

All chemicals were of reagent grade or better. Phenol,  $\text{KHSO}_5$ ,  $\text{CoSO}_4$ ,  $\text{KBr}$ ,  $\text{Na}_2\text{SO}_3$  and  $\text{N,N}$ -dimethyl-1,4-phenylenediamine monohydrochloride (DPD) were purchased from Aladdin (Shanghai, China). 2-bromophenol, 4-bromophenol, 2,4,6-tribromophenol were purchased from Sigma–Aldrich (St. Louis, MO). Methyl *tert*-butyl ether (MTBE) was HPLC grade and obtained from Fisher (Waltham, MA). Trihalomethanes (THMs) and haloacetic acids (HAAs) calibration mixtures were also purchased from Sigma–Aldrich. Individual stock solutions of phenol (2 mM),  $\text{KHSO}_5$  (500 mM),  $\text{CoSO}_4$  (0.5 mM),  $\text{KBr}$  (10 mM), DPD (8 mM), and  $\text{Na}_2\text{SO}_3$  (1 M) were prepared in reagent water from Millipore Super-Q water system and stored in the dark at 4 °C.

### 2.2. Batch reaction experiments

Batch reactions were conducted in a series of glass vials with headspace free at ambient temperature. The reaction solution contained 0.05 mM phenol and 0.2 mM  $\text{Br}^-$  with the absence and presence of 5  $\mu\text{M}$   $\text{Co}^{2+}$ . PMS doses of 1 and 5 mM were selected. Phosphate buffer (10 mM) was added to maintain pH 6.0. Reactions were initiated by adding appropriated volume of freshly prepared PMS stock solution to each of the vials to achieve preset concentrations. After the preset reaction time was reached, 3 vials were quenched by adding excess  $\text{Na}_2\text{SO}_3$  (1 M) and kept in the refrigerator until further treatment and analysis. One vial was for the analysis of bromide and  $\text{BrO}_3^-$ , the others for THMs and HAAs, respectively. All experiments were carried out in triplicates.

### 2.3. Kinetic assay

Kinetics were determined for the treatments with 0.05 mM phenol, 0.2 mM  $\text{Br}^-$ , 1.0 mM PMS both in the presence and absence of 5  $\mu\text{M}$   $\text{Co}^{2+}$ . Immediately after mixing, 1 mL reaction solution was transferred to a vial and placed in the autosampler tray of an Agilent 1200 high performance liquid chromatography (HPLC). The autosampler was programmed as withdrawing an aliquot of 10  $\mu\text{L}$  sample every 5 min from the same sampling vial and deliver it directly into the electron-spray ionization (ESI) source of an Agilent G6410B Triple Quad Mass Spectrometer. No LC separation was performed to avoid the decomposition of short-lived intermediate products. The ESI source was operated at negative mode and mass analyzer at full scan ( $m/z$  50–1000). Other instrumental setting were as follows: capillary voltage 4.0 kV, fragmentor 125 V, desolvation gas (nitrogen,  $\geq 99.995\%$ ) flow rate 10 mL/min, temperature 350 °C, nebulizer (nitrogen,  $\geq 99.995\%$ ) pressure 40 psi. The flow rate of the delivery solvent consisting of 50:50 methanol/water (v/v) was 0.2 mL/min. The dead time of the system was less than 0.05 min. Radical reactions were assumed fully quenched immediately after sampling since the delivery solvent containing 50% methanol. Thus, this approach allowed the acquisition of the mass spectra (MS) of the reaction solutions at selected time points. According to the characteristic isotopic signature endowed by the bromine atoms as well as molecular weights (MW), the brominated compounds could be tentatively identified in the MS. Data were continuously acquired for 2 h and the time-dependent concentration profiles of the brominated intermediates were constructed according to the change of their respective peak abundance.

Formation of free bromine was explored at the same conditions as described in the kinetic study. An aliquot of 1 mL sample was withdrawn from the reaction solution at every 5 min and immediately mixed with 1 mL DPD solution (8 mM). Free bromine was quantified colorimetrically by measuring the absorbance at 510 nm on a Varian Cary 50 spectrophotometer (APHA/AWWA/WEF, 2005). Controls with  $\text{Br}^-$  absent were also analyzed and the values were used to correct the absorbance created by oxidants other than free bromine. Standard deviation of this approach was within 5%.

### 2.4. Analysis of DBPs

THMs and HAAs were extracted with MTBE according to EPA Method 551.1 and 552.2, respectively. DBPs were analyzed using an Agilent 7890 gas chromatograph (GC) equipped with an electron capture detector (ECD) and HP-5 fused silica capillary column (30 m  $\times$  0.53 mm i.d., 1.5  $\mu\text{m}$  film thickness). Detailed analytical procedures and instrumental setup were specified in [Support Information](#). All the experiments were carried out in triplicates, and the data were averaged. The standard deviations were usually within 5–10% unless otherwise stated.

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