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Formation of halogenated disinfection byproducts during the degradation of chlorophenols by peroxymonosulfate oxidation in the presence of bromide

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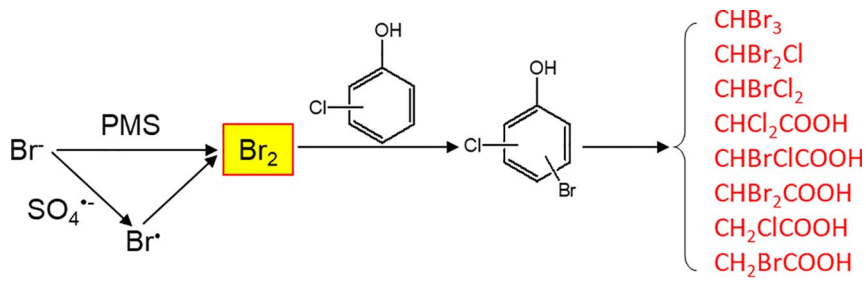
HIGHLIGHTS

- Br^- accelerated the degradation of chlorophenols in Co^{2+}/PMS and PMS oxidation processes.
- Br^- could be converted to free bromine by both $SO_4^{\cdot -}$ and PMS.
- Free bromine led to brominated intermediates and disinfection byproducts.
- Bromoform and dibromoacetic acid were the main DBPs in both systems.
- Bromodichloromethane and dichloroacetic acid were only detected in Br^-/Co^{2+}/PMS process.

GRAPHICAL ABSTRACT



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ABSTRACT

Advanced oxidation processes based on sulfate radical ($SO_4^{\cdot -}$) have obtained great attention in water treatment and *in-situ* ground water/soil remediation. In this study, the degradation of chlorophenols (CPs) in Co^{2+} activated peroxymonosulfate (PMS) oxidation process was explored. It was found that 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol could be effectively removed in Co^{2+}/PMS oxidation process. Presence of Br^- greatly accelerated the transformation of the CPs, which can be explained by the formation of reactive bromine species including both bromine radical species and free bromine from the oxidation of Br^- by $SO_4^{\cdot -}$. Br^- could also be oxidized by PMS directly to form free bromine. Thus, degradation of the CPs was also observed in PMS oxidation process without any activators in the presence of Br^-. Reactions between CPs and reactive bromine species resulted in the formation of brominated intermediates and disinfection byproducts (DBPs). Brominated phenolic intermediates such as Br_2Cl-CP, $BrCl_2$-CP, and Br_2Cl_2-CP were found in both Br^-/PMS and Br^-/Co^{2+}/PMS systems. However, oxidized intermediates such as Br_2Cl_2-quinones were only identified in Br^-/Co^{2+}/PMS system. $SO_4^{\cdot -}$ and radical bromine species are believed to be responsible for the formation of oxidized products. Bromoform and dibromoacetic acid were the main DBPs in both Br^-/Co^{2+}/PMS and Br^-/PMS processes. Dichlorinated DBPs species, such as $CHBrCl_2$ and dichloroacetic acid, were only found in Br^-/Co^{2+}/PMS system. Formation of dichlorinated DBPs suggests both dechlorination and chlorination reactions occurred, during which $SO_4^{\cdot -}$ played a key role. The findings of this study indicate that presence of Br^- can significantly facilitate the removal of organic contaminants but lead to brominated DBPs in PMS oxidation process, which should be taken into consideration when PMS is applied in environmental matrices containing Br^-.

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1. Introduction

Chlorophenols (CPs), such as 2-chlorophenol (MCP), 2,4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP), and pentachlorophenol (PCP), are used as wood preservatives, pesticides, and defoliants since early 1930s [39,40]. They are also important intermediates in the synthesis of chlorophenoxy acid herbicides and other important organic substances [50]. CPs can be found in different environmental compartments, such as rivers, lakes, sediments, ambient air, soils, and landfill leachates [7], [50]. TCP is also formed as a byproduct in water chlorinated processes [36,48]. Due to their high toxicity, carcinogenicity, and persistence, much attention has been paid to their occurrence in the environment and risks associated to their presence. CPs are listed as priority pollutants by regulatory agencies of the United States, China, and many other countries [14,25,33,41,46,50].

Many technologies have been developed to eliminate CPs in the environment [3,40,46]. It has been reported that CPs could be efficiently removed by advanced oxidation processes (AOPs) based on hydroxyl radical ($HO^{\cdot}$), such as UV/H_2O_2, Fenton, and UV/O_3 [4,8]. Recently, AOPs based on sulfate radical ($SO_4^{\cdot -}$) have obtained considerable attention in the treatment of industrial wastewaters and *in-situ* soil/ground water remediation [11,16,23]. $SO_4^{\cdot -}$ can be generated via scission of the peroxide bond of peroxymonosulfate (PMS) or persulfate (PS) by heat, UV, or transition metals [1,2,22]. $SO_4^{\cdot -}$ is a single electron oxidant with a redox potential of 2.5–3.1 V (depending on the pH) which is comparable to that of $HO^{\cdot}$ (2.7 V in acid solution and 1.8 V in neutral solution) [5]. Sulfate radical-based AOPs (SR-AOPs) have shown success in the treatment of a wide range of organic contaminants, including polychlorinated biphenyls [12], pesticides [23], antibiotics [9,16,21,52], endocrine disrupting chemicals [51]. Removal of CPs in SR-AOPs has also been documented. It was reported that TCP could be efficiently degraded by $SO_4^{\cdot -}$ in Co^{2+}/PMS and UV/PMS systems [17,47].

However, few researches have examined the transformation and fate of chlorine during the degradation of CPs in SR-AOPs. In a previous study, we demonstrated that the degradation of tetrabromobisphenol A (TBBPA) in Co^{2+}/PMS oxidation process led to the formation of brominated byproducts such as bromoform and bromoacetic acids (BAAs) [20]. During this process, the bromine in TBBPA molecule was not mineralized but transformed to other organic forms. Hence, removal of TBBPA in $SO_4^{\cdot -}$ oxidation process does not necessary mean the elimination ofenvironmental risks. Instead, these brominated byproducts, also known as disinfection byproducts (DBPs), are highly toxic and regulated globally [43,48]. Formation of brominated DBPs was attributed to the capability of $SO_4^{\cdot -}$ to oxidize bromide ($E^0_{Br\cdot/Br^-} = 1.62$ V) to reactive bromine species including bromine radicals ($Br^{\cdot}$, $Br_2^{\cdot -}$) and free bromine (Br_2, HBrO) which reacted with other organic compounds in the solution to form brominated DBPs [20]. Several papers reporting the formation of brominated DBPs in SR-AOPs in the presence of Br^- have been published recently [27,28,30,45]. In the case of TBBPA, the Br^-, although not present initially, could be *in situ* formed from the degradation of TBBPA.

Chloride ($E^0_{Cl\cdot/Cl^-} = 2.41$ V) is presumed to be oxidized by $SO_4^{\cdot -}$ to form reactive chlorine species in a similar way [19]. It was proposed that the organic chlorine was transformed to Cl^- which could be oxidized by $SO_4^{\cdot -}$ subsequently and converted to organic chlorine again during the degradation of CPs by $SO_4^{\cdot -}$ [1,10]. This means that chlorinated byproducts can also be generated during the degradation of organochlorines by $SO_4^{\cdot -}$. For example, trichlorophenol and pentachlorophenol were identified during degradation of DCP in Co^{2+}/PMS oxidation process [1]. Fang et al. [11] observed the formation of absorbable organic halogen (AOX) during the degradation of TCP in Co^{2+}/PMS process; while presence of Cl^- resulted in increased AOX formation. Similar increased AOX formation was also documented in the degradation of monochlorophenols by $SO_4^{\cdot -}$ in the presence of Cl^- [10]. Nonetheless, the chlorinated compounds identified in earlier works are only intermediates. They are to be further transformed in the presence of $SO_4^{\cdot -}$. Few efforts have been made to investigate the formation and transformation of these chlorinated products systematically. In addition, in the presence of Br^-, halogenated byproducts having both chlorine and bromine incorporated will be formed. In order to test these hypotheses, transformation of MCP, DCP, and TCP in Co^{2+} activated PMS oxidation process was examined. Particular attention was paid to the influence of Br^- on the degradation of the CPs and formation of halogenated byproducts. We believe the results of this study are of relevance in assessing the feasibility of SR-AOPs in the decontamination of chlorinated pollutants.

2. Materials and methods

2.1. Reagents and materials

All chemicals were of analytical grade or better. MCP, DCP, TCP, PMS, KBr, $CoSO_4$, and Na_2SO_3 were purchased from Aladdin (Shanghai, China). Trihalomethanes (THMs) and haloacetic acids (HAAs) calibration standards were obtained from Sigma Aldrich (St. Louis, MO). HPLC grade methyl tert-butyl ether (MTBE), dichloromethane, and methanol were supplied by Burdich & Jackson (Shanghai, China). Stock solutions of PMS, KBr, chlorophenols were prepared by dissolving appropriate amount of the reagents in Milli-Q water (18.2 MΩ/cm).

2.2. Kinetic study

Degradation of MCP, DCP and TCP in Co^{2+}/PMS system in the presence of 0.1 mM Br^- was performed individually in a series of 42-mL EPA vials at room temperature (25 ± 1 °C). Reaction solution contained 0.05 mM of an individual CP, 0.1 mM Br^-, and 1 mM PMS initially. Phosphate buffer (10 mM) was added to maintain pH 6.5 in order to mimic real environmental conditions. Pre-experiment showed that the removal of CPs was not affected by the presence of buffer species. A certain amount of $CoSO_4$ was added finally to initiate the reaction. $CoSO_4$ concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 μM were tested. The solution was magnetically stirred to insure homogeneity during the reaction. At pre-selected time interval, an aliquot of 900 μL solution was withdrawn from each of the reactors and immediately transferred to the sampling vials preloaded with 100 μL Na_2SO_3 (100 mM) as the quenching agent. Pre-experiment showed that no further change of CPs concentrations occurred after quenching by Na_2SO_3. The samples were placed in a refrigerator at 4 °C until further analysis for the residual CPs. Control experiments without Br^- or $CoSO_4$ or neither of them was also performed.

Residual CPs in the samples were measured by a Hitachi L-2000 high performance liquid chromatography (HPLC, Hitachi, Japan) equipped with an L-2455 diode array detector. The separation was carried out on an Agilent Zorbax Eclipse Plus C18 reverse phase column (250 mm × 4.6 mm i.d., 5 μm particle size) at 40 °C using a gradient composition of methanol (solvent A) and water (solvent B) (0.1% acetic acid) as mobile phases. The gradient expressed as changes in solvent A was as follows: 0–8 min, a linear increase from 60% to 95%; 8–11 min, hold at 95% A; 11–11.5 min, a liner decrease from 95% to 60%; 11.5–13 min, hold at 60% A. The flow rate was 1 mL/min and the injection volume was 20 μL. The quantification was based on absorbance at 275 nm which corresponds to the peak of absorbance band of CPs. Quantification was based on multipoint standard calibration curves. The standard deviations were usually within 5–10% unless otherwise stated.

2.3. Analysis of transformation intermediates

Transformation intermediates and products of CPs in Co^{2+}/PMS oxidation process in the presence of Br^- was enriched by liquid-liquid