



## Short communication

## Sulfate radical-induced degradation of 2,4,6-trichlorophenol: A de novo formation of chlorinated compounds

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## HIGHLIGHTS

- Sulfate radicals can efficiently degrade 2,4,6-trichlorophenol (TCP) in Co/PMS system.
- pH and its adjustment order largely affect TCP degradation kinetics.
- A de novo formation mechanism of polychlorinated compounds was proposed.

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## ABSTRACT

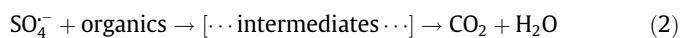
The degradation of 2,4,6-trichlorophenol (TCP) by sulfate radical generated via Co(II)-mediated activation of peroxymonosulfate (PMS) was examined. The influencing factors, such as substrate concentration and pH were investigated. The initial pH and its adjustment orders significantly affected the TCP degradation and mineralization. Several chlorinated products were detected, as well as some carboxylic acids, such as glycolic acid and oxalic acid. Many polychlorinated (chlorine atom number  $\geq 3$ ) aromatics (e.g. 2,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol, 2,3,5,6-tetrachloro-1,4-benzenediol) and even their ring-opening products (e.g. 2,4-dichloro-5-oxo-2-hexenedioic acid, 1,1,3,3-tetrachloro-2-propanone) were identified, indicating a de novo formation mechanism of organohalogens may be involved in TCP degradation. The released chlorine atoms from TCP and/or dichloride radicals activated by sulfate radicals played an important role. This finding may have significant scientific and technical implications for utilizing Co/PMS reagent to detoxify chlorinated pollutants.

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## 1. Introduction

Advanced oxidation processes (AOPs) based on highly reactive hydroxyl radicals ( $\cdot\text{OH}$ ), have been found to oxidize the chlorinated phenolic compounds efficiently [1–3]. However, it is widely recognized that hydroxyl radicals are effective only under acidic conditions in most cases. Compared to  $\cdot\text{OH}$ , the sulfate radical ( $\text{SO}_4^{\cdot-}$ ) has a higher standard redox potential (2.5–3.1 V versus NHE) with a wide pH range (2.0–8.0) and thus has attracted more attention recently in the degradation of many organic contaminants, such as azo-dyes, 2,4-dichlorophenoxyacetic acid (2,4-D) and chlorinated compounds [4–8].  $\text{SO}_4^{\cdot-}$  can completely oxidize a majority of organic pollutants, especially poorly biodegradable pollutants which are present in wastewater or convert them into simple biodegradable compounds [5,7]. Co(II)-mediated decomposition of peroxymono-

sulfate ( $\text{KHSO}_5$ , PMS) has been proved to be the most efficient method to generate  $\text{SO}_4^{\cdot-}$  via the following reactions [6,8]:



The degradation of 2,4,6-trichlorophenol (TCP), recognized as one of the priority pollutants by US EPA, has been examined so far in  $\text{O}_3$ , UV,  $\text{H}_2\text{O}_2$ , Fenton, photocatalytic degradation processes [3,9–12]. To our best knowledge, there are no literatures available regarding the  $\text{SO}_4^{\cdot-}$ -induced degradation of TCP. It is still unknown that whether the sulfate radical can effectively detoxify TCP to biodegradable organic compounds. Also whether the released  $\text{Cl}^-$  from dechlorination can be involved in the re-chlorination (de novo formation) activated by sulfate radical is worthy of investigations, since our recent studies [4,7] indicated that the co-existing inorganic chloride ions could be chemically converted to organohalogen via both non-radical two electron-transfer pathway and  $\text{SO}_4^{\cdot-}$ -based reactions (Eqs. (3)–(12)).

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