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# Kinetic and mechanistic insights into the degradation of clofibric acid in saline wastewater by $\text{Co}^{2+}$ /PMS process: a modeling and theoretical study†

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Recently, the degradation of non-chlorinated organic pollutants in saline pharmaceutical wastewater by  $\text{SO}_4^{\bullet-}$ -based advanced oxidation processes (AOPs) has received widespread attention. However, little is known about the oxidation of chlorinated compounds in  $\text{SO}_4^{\bullet-}$ -based AOPs. This study chose clofibric acid (CA) as a chlorinated pollutant model; the oxidation kinetics and mechanistic pathway were explored in the  $\text{Co}^{2+}$ /peroxymonosulfate (PMS) system. Notably, a high removal efficiency (81.0%) but low mineralization rate (9.15%) of CA within 120 min were observed at pH 3.0 during  $\text{Co}^{2+}$ /PMS treatment. Exogenic  $\text{Cl}^-$  had a dual effect (inhibitory then promoting) on CA degradation. Several undesirable chlorinated by-products were formed in the  $\text{Co}^{2+}$ /PMS system. This demonstrated endogenous chlorine and exogenic  $\text{Cl}^-$  both reacted with  $\text{SO}_4^{\bullet-}$  to generate chlorine radicals, which participated in the dechlorination and rechlorination of CA and its by-products. Furthermore,  $\text{SO}_4^{\bullet-}$  was the dominant species responsible for CA degradation at low  $\text{Cl}^-$  concentrations ( $\leq 1$  mM), whereas  $\text{Cl}_2^{\bullet-}$  was the predominant radical at  $[\text{Cl}^-]_0 > 1$  mM. A possible degradation pathway of CA was proposed. Our findings suggested that chlorinated compounds in highly saline pharmaceutical wastewater will be more resistant and deserve more attention.

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## 1 Introduction

It is well known that pharmaceutical industries produce a large amount of toxic and hazardous wastewater, characterized by high biological oxygen demand (BOD), chemical oxygen demand (COD), salinity, and toxicity.<sup>1</sup> Pharmaceutical wastewater has severe adverse impacts on aquatic environments and requires pretreatment before discharge.<sup>2,3</sup> Clofibric acid (CA), a stable pharmaceutical contaminant with potential ecosystem and human health risks, is persistent and has been commonly detected in aquatic environments.<sup>4,5</sup> Due to its complex structure, CA removal was limited to traditional biological degradation.<sup>6</sup> Currently, advanced oxidation processes (AOPs) show stronger oxidation abilities to refractory contaminants and have been extensively applied in CA degradation, such as UV/ $\text{O}_3$ ,<sup>7</sup> UV/ $\text{TiO}_2$ ,<sup>8</sup> and UV/ $\text{O}_3$ /peroxydisulfate (PDS).<sup>9</sup> Among these methods,  $\text{SO}_4^{\bullet-}$ -based AOPs have garnered substantial scientific interest.<sup>9</sup>

Typically,  $\text{SO}_4^{\bullet-}$  is extremely reactive towards a wide range of organic compounds with redox potentials between 2.5–3.1 V.

Furthermore,  $\text{SO}_4^{\bullet-}$  tends to react with organic compounds *via* one-electron transfer rather than addition or H abstraction, which are less influenced by water matrix components.<sup>9</sup> Peroxymonosulfate (PMS) is an efficient precursor of  $\text{SO}_4^{\bullet-}$  and activated by transition metals,<sup>10</sup> UV radiation,<sup>11</sup> heat,<sup>12</sup> ultrasound,<sup>13</sup> and others. Among those methods,  $\text{Co}^{2+}$  is the most efficient transition-metal ion for PMS activation, leading to radical-induced contaminant oxidation.<sup>14</sup>  $\text{Co}^{2+}$ /PMS has been universally recognized as a  $\text{SO}_4^{\bullet-}$ -based system *via* one-electron oxidation.<sup>15</sup> However, recent studies indicated a two-electron transfer pathway involving a non-radical route (*i.e.*,  $\text{Co}^{4+}$ ) occurred at pH = 3.0 in the  $\text{Co}^{2+}$ /PMS system.<sup>16,17</sup> To date, the main reactive oxygen species (ROS), involving radical and non-radical pathways, and their contributions to CA degradation affected by water constituents (*i.e.*, inorganic ions) in the  $\text{Co}^{2+}$ /PMS system were overlooked.

Chloride ion ( $\text{Cl}^-$ ) is ubiquitous in industrial wastewater, whereas the impacts of exogenic  $\text{Cl}^-$  (inorganic form from a water matrix) in oxidations of different chlorinated organic compounds in the  $\text{Co}^{2+}$ /PMS system are still controversial due to the complicated reaction process. For example, Anipsitakis *et al.*<sup>18</sup> reported a facilitating effect of low dosage  $\text{Cl}^-$  on the degradation of 2,4-dichlorophenol in the  $\text{Co}^{2+}$ /PMS system. Chan and Chu *et al.*<sup>19</sup> found the presence of  $\text{Cl}^-$  (0–6.8 mM) significantly restrained the removal efficiency and reduced the

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reaction rate of atrazine. A dual impact (inhibitory then promoting) of  $\text{Cl}^-$  (0–500 mM) was reported in the oxidative degradation of 4-chloro-2-nitrophenol by  $\text{Co}^{2+}$ /PMS.<sup>20</sup> Hence, the concentration of exogenic  $\text{Cl}^-$ , as well as substrate properties might be significant in chlorinated organic compound oxidations in AOPs. Currently, some groups have investigated the influence of exogenic  $\text{Cl}^-$  on the degradation efficiency of CA in AOPs.<sup>9,21</sup> Qin *et al.*<sup>9</sup> pointed out that degradation of CA in the UV/ $\text{O}_3$ /PDS system dropped slightly as the  $\text{Cl}^-$  concentration increased from 0 to 10 mM. Tang *et al.*<sup>21</sup> reported that a  $\text{Cl}^-$  concentration increase (0–2 mM) promoted CA degradation in the UV/ $\text{Cl}^-$  system. However, the effect of exogenic  $\text{Cl}^-$  on CA degradation in the  $\text{Co}^{2+}$ /PMS system was not thoroughly examined, especially under highly saline conditions.

In addition to the effect of exogenic  $\text{Cl}^-$  ions in highly saline wastewater on CA removal, the significance of endogenic  $\text{Cl}^-$  (organic form from the contaminant itself) on the degradation process of CA was also neglected. Endogenic  $\text{Cl}^-$  from chlorinated organic pollutants played an important role in dehalogenation and halogenation processes. Dechlorination was observed during chlorobenzene oxidation with  $\text{SO}_4^{\cdot-}$ .<sup>22,23</sup> The chlorine atoms released from the benzene ring participated in *de novo* formation of chlorinated by-products by  $\text{SO}_4^{\cdot-}$ ,<sup>24</sup> which led to the formation of polychlorinated aromatics during 2,4,6-trichlorophenol (TCP) oxidation.<sup>25</sup> However, previous studies have mainly focused on the oxidation efficiency and degradation pathways of CA in AOPs,<sup>7–9</sup> and little attention has been paid to the dechlorination and rechlorination of endogenic  $\text{Cl}^-$  during CA oxidation.

This study aims to: (1) evaluate the influence of exogenic  $\text{Cl}^-$  on the degradation kinetics of CA; (2) explore the transformation of endogenic chlorine of CA during  $\text{Co}^{2+}$ /PMS treatment; (3) investigate the conversion of reactive oxygen species and their contributions to CA degradation; (4) explore the oxidation mechanisms and propose a possible degradation pathway of CA. This work hopes to provide valuable information for studying the role of exogenic  $\text{Cl}^-$  in the oxidation of chlorinated compounds in pharmaceutical wastewater.

## 2 Experimental

### 2.1 Materials

Clofibric acid ( $\text{C}_{10}\text{H}_{11}\text{ClO}_3$ , >99%), acid orange 7 (AO7,  $\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_4\text{SNa}$ , >98%), and carbamazepine (CBZ,  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$ , 98%) were obtained from Acros Organics. Oxone® ( $[\text{2KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4]$  salt, 95%), L-histidine and hexamethyldisilazane, pyridine, and chlorotrimethylsilane were obtained from Sigma-Aldrich. HPLC grade acetonitrile and methanol were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methyl phenyl sulfoxide (PMSO) and methyl phenyl sulfone (PMSO<sub>2</sub>) were obtained from Shanghai Rhawn Chemical Technology Co., Ltd.  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NaNO}_2$ ,  $\text{NaCl}$ ,  $\text{NaOH}$ , and  $\text{H}_2\text{SO}_4$  were of analytical grade, and used without further purification. Milli-Q water (Millipore, France, >18.2 MΩ cm) was used to prepare all reagents and solvents.

### 2.2 Experimental procedure

All reactions were performed in a 50 mL glass beaker and magnetically stirred (300 rpm) at room temperature ( $25 \pm 2^\circ\text{C}$ ). Reactions were initiated by mixing a specific concentration of PMS into a solution containing CA,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , or other chemicals without pH control. While the effect of pH on the removal efficiency of CA was also studied,  $\text{NaOH}$  or  $\text{H}_2\text{SO}_4$  adjusted the pH of the mixed solution to the desired level. Samples were taken at predetermined times for analysis and quenched with methanol (for HPLC) or  $\text{NaNO}_2$  (for GC-MS and TOC). All tests were conducted in duplicate to ensure reproducibility and the data are shown as averages with error bars ( $\pm 5\%$ ).

### 2.3 Analytical methods

Residual CA and CBZ concentrations were measured by a Waters e2695 with 2489 UV/Vis detector using an Atlantis® T3 Waters column ( $4.6 \text{ mm} \times 250 \text{ mm}$ ,  $5 \mu\text{m}$ ) at 227 and 210 nm, respectively. The mobile phase for CA detection contained 0.5% phosphoric acid/methanol (15/85 (v/v)) at a flow rate of  $1.0 \text{ mL min}^{-1}$ . The sample injection volume was  $20 \mu\text{L}$ . AO7 concentrations were measured by a Hitachi F-4600 spectrophotometer (Hitachi, Japan) at 485 nm. PMS concentrations were detected spectrophotometrically by iodometric titration at 352 nm.<sup>26</sup> A Shimadzu TOC analyzer (TOC-VCPH, Shimadzu, Japan) measured the total organic carbon (TOC). The intermediates of CA were analyzed by GC-MS, (Agilent 8860-GC/5977B-MSD, USA) and the detailed operational parameters are provided in Text S1.†

The oxidation of clofibric acid under various conditions was modeled using pseudo-first-order kinetics eqn (1)

$$C/C_0 = e^{-kt} \quad (1)$$

where  $C_0$  and  $C$  are the concentrations of CA at  $t = 0$  and  $t$  min, respectively,  $k$  is the pseudo-first-order rate constant ( $\text{min}^{-1}$ ), and  $t$  is the reaction time.

### 2.4 Kinetic modeling

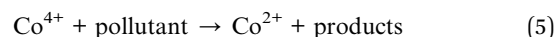
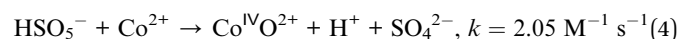
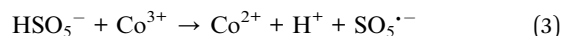
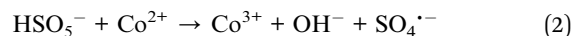
Kinetic modeling of the  $\text{Co}^{2+}$ /PMS system was performed by *Kintecus* 6.51 (<https://www.kintecus.com>). All radical reactions used as input for kinetic modeling were listed in Table S1.† The formations and transformations of reactive species such as the hydroxyl, sulfate, and chlorine radicals were simulated according to the reactions in Table S1.† Most reaction rate constants were obtained from previous studies,<sup>27–29</sup> while some unknown reaction rate constants were calculated by fitting the traces of CA degradation curves by taking these unknown rate constants as adjustable. Due to negligible production at pH 3.0, reactions of chlorite/chlorate were not included in our model.<sup>30</sup> Unknown or poorly-defined parameters were optimized to accurately simulate species distributions by using a numerical procedure associated with *Kintecus* programs.

### 3 Results and discussion

#### 3.1 CA degradation

**3.1.1 Effect of  $\text{Co}^{2+}$  concentration.**  $\text{Co}^{2+}$  played an important role as a catalyst in the  $\text{Co}^{2+}$ /PMS system. The impacts of catalyst levels on CA degradation were studied and the degradation kinetics and impacts on the rate constant  $k$  are shown in Fig. S1a† and 1a, respectively. No CA oxidation was observed without  $\text{Co}^{2+}$  addition (Fig. S1a†), which suggested CA was not oxidized by PMS itself. Furthermore, CA degradation rates increased significantly with  $\text{Co}^{2+}$  concentration increased (Fig. 1a). The reaction rate constant  $k$  increased from 0 to  $3.36 \times 10^{-2} \text{ min}^{-1}$  as  $\text{Co}^{2+}$  increased from 0 to 0.3 mM. Dramatic degradation rates and oxidation efficiencies were detected at  $[\text{Co}^{2+}]_0 < 0.02 \text{ mM}$ , whereas no obvious enhancement was obtained when the  $\text{Co}^{2+}$  concentration increased from 0.02 to 0.3 mM. This may be due to  $\text{Co}^{2+}$  inducing rapid PMS decomposition with the highest efficiency to generate  $\text{SO}_4^{\bullet-}$  (eqn (2)). The regeneration of  $\text{Co}^{2+}$  with excess PMS ( $E^0(\text{Co}^{3+}/\text{Co}^{2+}) = 1.45 \text{ V}$ ) may be a vital step to continue catalysis at low  $\text{Co}^{2+}$  levels ( $\leq 0.02 \text{ mM}$ ) (eqn (3)).<sup>28</sup> Moreover, the non-radical  $\text{Co}^{4+}$  could also exist in the  $\text{Co}^{2+}$ /PMS system at pH 3.0 (as seen in eqn (4)) and more  $\text{Co}^{4+}$  may form at higher  $\text{Co}^{2+}$  dosages.<sup>16</sup>  $\text{Co}^{4+}$  could react with the target pollutant to regenerate  $\text{Co}^{2+}$  via eqn (5) and participate in the next oxidation cycle. Notably, the maximum degradation rate appeared when  $\text{Co}^{2+}$  concentration increased

to 0.3 mM, revealing that 0.5 mM PMS was not completely consumed and continued to produce radicals. Xue *et al.* also reported a similar phenomenon during thiamphenicol (TAP) and florfenicol (FFC) in the  $\text{Co}^{2+}$ /PMS system.<sup>31</sup> In this study, the optimal dosage of  $\text{Co}^{2+}$  was 0.01 mM with an appropriate degradation efficiency (81.0%) and a high rate constant  $k$  ( $3.21 \times 10^{-2} \text{ min}^{-1}$ ).



**3.1.2 Effect of PMS concentration.** The impact of initial PMS concentration on CA degradation in the  $\text{Co}^{2+}$ /PMS system was studied. As illustrated in Fig. 1b, at PMS concentrations between 0–10 mM, the rate constant of CA degradation increased from 0 to  $6.56 \times 10^{-2} \text{ min}^{-1}$ . Higher levels of PMS accelerated the formation of reactive oxygen species, and the degradation efficiency of CA was proportional to the oxidant dosages under the same catalyst dosage (eqn (2) or eqn (4)). The rate constant increased rapidly when PMS was 0–1 mM, while only a slight improvement was observed at PMS concentrations

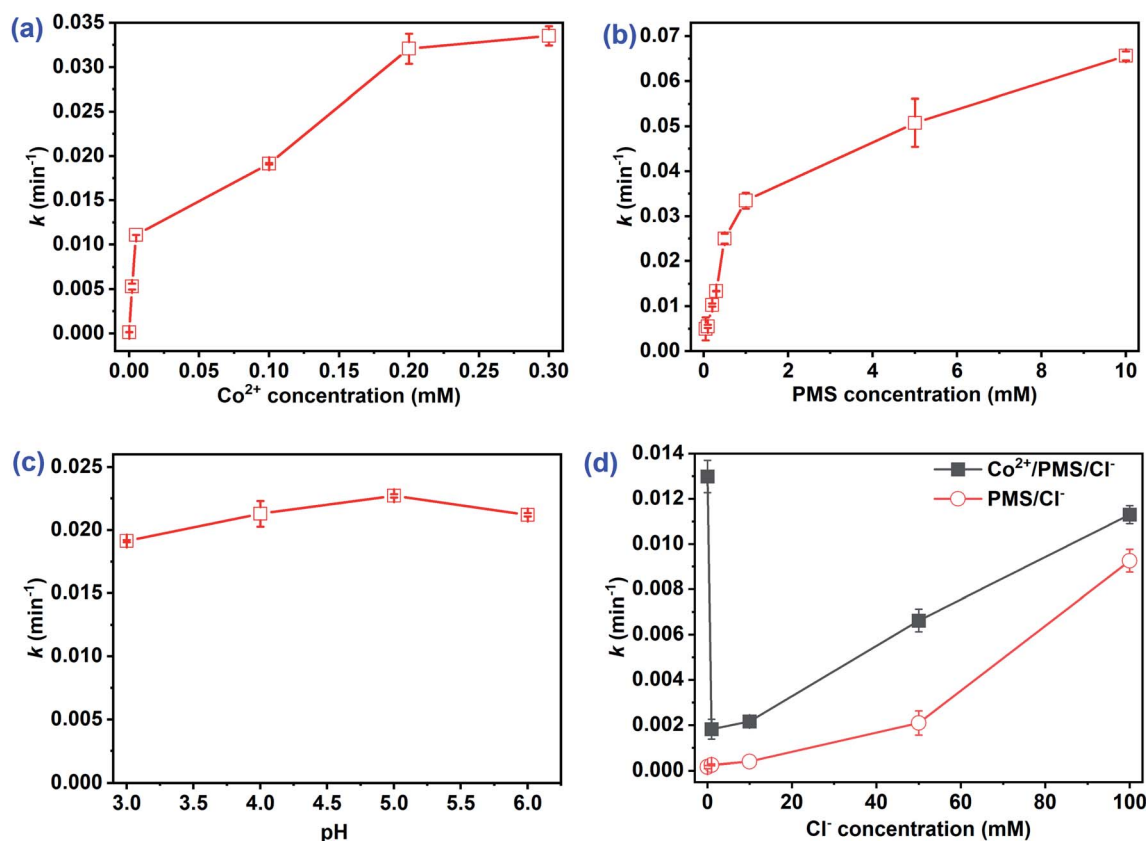
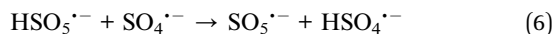


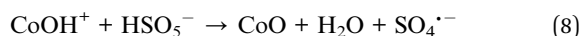
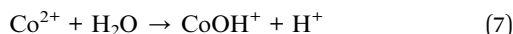
Fig. 1 Effect of initial (a)  $\text{Co}^{2+}$  concentration, (b) PMS concentration, (c) pH, and (d)  $\text{Cl}^-$  concentration on the rate constants  $k$  of CA. Experimental conditions:  $[\text{CA}]_0 = 0.1 \text{ mM}$ , (a, b, d) pH = 3.0; (a, c, d)  $[\text{PMS}]_0 = 0.5 \text{ mM}$ ; (b, c, d)  $[\text{Co}^{2+}]_0 = 0.01 \text{ mM}$ .



above 1 mM. Wang *et al.*<sup>10</sup> revealed excessive PMS acted as a radical scavenger, which accelerated the conversion of  $\text{SO}_4^{\cdot-}$  to less reactive  $\text{SO}_5^{\cdot-}$  (eqn (6)). Increasing the PMS concentration to 10 mM, the low concentration of  $\text{Co}^{2+}$  limited ROS production, which led to the slight degradation rate enhancement. Notably, the degradation efficiency of CA increased gradually when  $[\text{PMS}]_0 < 0.5$  mM, whereas no evident depletion of CA was obtained at PMS concentrations between 0.5–10 mM (Fig. S1b†). Therefore, 0.5 mM was selected as the optimal PMS concentration.

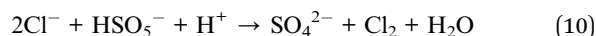
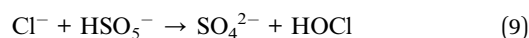


**3.1.3 Effect of pH.** The solution pH played a vital role in organic degradation as well as ROS formation in the  $\text{SO}_4^{\cdot-}$ -based AOP system.<sup>31,32</sup> Notably, the CA concentration was not detected by HPLC under neutral or alkaline conditions (Fig. S2†). Due to the strong oxidation capability of PMS under alkaline conditions,<sup>28</sup> the impact of initial pH 3.0 to 6.0 was examined. As shown in Fig. 1c, the rate constants at pH levels of 3.0, 4.0, 5.0, and 6.0 were  $1.91 \times 10^{-2}$ ,  $2.13 \times 10^{-2}$ ,  $2.27 \times 10^{-2}$ , and  $2.12 \times 10^{-2} \text{ min}^{-1}$ , respectively. Fig. 1c indicated the rate constant increased slightly at pH levels between 3.0–5.0 in the  $\text{Co}^{2+}$ /PMS system. It is worth noting that  $\text{HSO}_5^-$  and  $\text{Co}^{2+}$  were the dominant forms of PMS and  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  at  $\text{pH} < 6.0$ .<sup>10</sup> Additionally, higher pH levels assisted the formation of  $\text{CoOH}^+$  via  $\text{Co}^{2+}$  hydrolysis (eqn (7)) and was the predominant species responsible for PMS decomposition (eqn (8)).<sup>33</sup> The rate constant dropped slightly as the pH increased from 5.0 to 6.0, possibly due to HPLC measurement errors as the pH approached neutral or alkaline conditions (Fig. S2†). A similar phenomenon was obtained for the oxidation of TCP<sup>25</sup> and FFC.<sup>31</sup> Although the rate constant optimized at  $\text{pH} = 5.0$ , the degradation efficiency (78.0%) decreased slightly after 120 min as compared to  $\text{pH} 3.0$  (81.0%). Thus, an initial  $\text{pH} = 3.0$  without adjustment was applied in the following experiments.



**3.1.4 Effect of  $\text{Cl}^-$  concentration.** Pharmaceutical wastewater usually contains many salts, which may influence the oxidation efficiency of pharmaceutical contaminants. Thus, the impact of chloride ions on CA degradation was investigated. As illustrated in Fig. 1d,  $\text{Cl}^-$  had a dual effect (inhibitory then promoting) on the CA degradation. Low  $\text{Cl}^-$  concentrations ( $\leq 1$  mM) had a negative impact on CA oxidation, but facilitated oxidation when  $[\text{Cl}^-]_0 > 1$  mM (Fig. S3a†). The chloride ion was supposed to scavenge  $\text{SO}_4^{\cdot-}$  to generate less reactive chlorine radicals ( $\text{Cl}^\cdot/\text{Cl}_2^{\cdot-}$ ), and lead to the inhibitory effect of  $\text{Cl}^-$  on CA degradation.<sup>34</sup> Further addition of chloride and formation of chlorine species ( $\text{HOCl}/\text{Cl}_2$ ) shown in eqn (9) and (10) may facilitate rapid CA degradation.<sup>35</sup> For comparison, removal of AO7 and CBZ under the same conditions was also studied. As

shown in Fig. S4,† a similar phenomenon (inhibitory then promoting) was observed and critical points also appeared at low  $\text{Cl}^-$  concentrations. Moreover, the same dual effect of  $\text{Cl}^-$  was observed for 4-chloro-2-nitrophenol removal in saline wastewater by  $\text{Co}^{2+}$ /PMS,<sup>20</sup> whereas an opposite dual effect (promoting then inhibitory) was obtained on chlorinated azo dye oxidation in the UV/PS system.<sup>36</sup> However, CA degradation efficiency gradually increased with added  $\text{Cl}^-$  in the PMS/ $\text{Cl}^-$  system (Fig. S3b†). The removal rate of CA was 75.1% after 120 min in the presence of 100 mM  $\text{Cl}^-$  by PMS/ $\text{Cl}^-$  but reached 85.4% when  $\text{Co}^{2+}$  and  $\text{Cl}^-$  coexisted. According to previous studies, PMS can oxidize  $\text{Cl}^-$  directly to generate reactive chlorine species ( $\text{HClO}/\text{Cl}_2$ ) to degrade organic compounds.<sup>35</sup> However, this dual effect of  $\text{Cl}^-$  was not present in  $\text{H}_2\text{O}_2$ -based AOPs, such as Fenton and photo-Fenton systems,<sup>37</sup> because  $\text{Cl}^-$  cannot activate  $\text{H}_2\text{O}_2$  to oxidize the contaminants.



## 3.2 Mineralization

The mineralization of CA was evaluated by measuring TOC removal efficiency. As depicted in Fig. 2, the mineralization rate increased with prolonged reaction times, while TOC removal in the  $\text{Co}^{2+}$ /PMS system was much higher than in the absence of  $\text{Co}^{2+}$ . TOC removal was 3.09% and 9.15% with 0 mM  $\text{Cl}^-$  in the  $\text{Co}^{2+}$ /PMS system after 30 and 120 min, respectively. However, the mineralization degree of CA was 2.24%, and 1.69% after 120 min at 1 mM, and 100 mM  $\text{Cl}^-$  in the  $\text{Co}^{2+}$ /PMS system, respectively. TOC removal decreased with additional  $\text{Cl}^-$  in the  $\text{Co}^{2+}$ /PMS system. Interestingly, the degradation efficiency of CA improved at high  $\text{Cl}^-$  (300 mM) in the PMS/ $\text{Cl}^-$  system

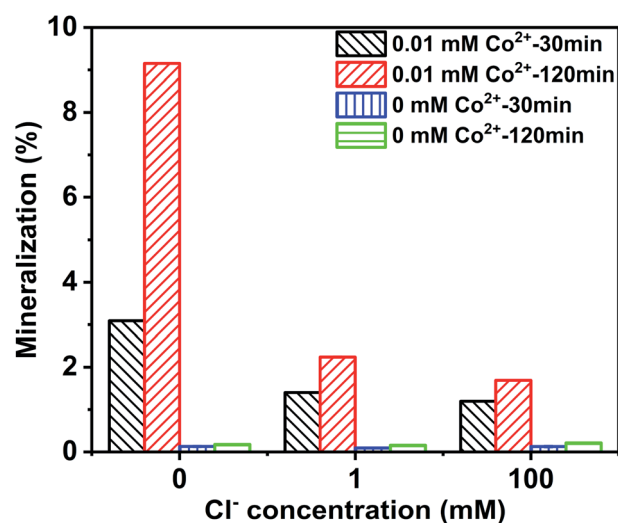


Fig. 2 Mineralization of CA degradation with different  $\text{Cl}^-$  concentrations at different reaction times in the  $\text{Co}^{2+}$ /PMS/ $\text{Cl}^-$  and PMS/ $\text{Cl}^-$  system, respectively. Experimental conditions:  $[\text{CA}]_0 = 0.1$  mM,  $[\text{Co}^{2+}]_0 = 0.01$  mM,  $[\text{PMS}]_0 = 0.5$  mM,  $\text{pH} 3.0$ .

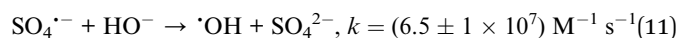




(Fig. S3b†) but the TOC removal rate was lower than 0.2%. In general, the mineralization degree of CA was quite low in the  $\text{Co}^{2+}$ /PMS system. The high degradation efficiency but low mineralization degree of CA suggested the formation of refractory intermediates in a saline environment, especially chlorinated by-products.<sup>38</sup>

### 3.3 Free radical identification

$\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  are regarded as the primary radicals yielded in PMS-based systems.<sup>34,39</sup> Hence, quenching experiments were conducted to detect the major ROS during the oxidation of organic pollutants in AOPs. Both  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  were scavenged by methanol (MeOH) with the rate constants of  $9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. *tert*-Butyl alcohol (TBA) reacts with  $\cdot\text{OH}$  ( $k_{\text{TBA}, \cdot\text{OH}} = (3.8-7.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), but not  $\text{SO}_4^{\cdot-}$  ( $k_{\text{TBA}, \text{SO}_4^{\cdot-}} = (4.0-9.1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>40,41</sup> In the absence of  $\text{Cl}^-$ , as shown in Fig. 3a, 20 mM TBA had almost no influence on CA degradation, while the degradation rate of CA decreased from 81.0% to 66.0% by adding 1 M TBA. In contrast, MeOH inhibited CA degradation. Adding 20 mM MeOH reduced the degradation rate of CA from 81.0% to 34.8%, and CA removal stopped completely when 1 M MeOH was added. This result indicated that  $\text{SO}_4^{\cdot-}$  was the primary oxidant in the  $\text{Co}^{2+}$ /PMS system without  $\text{Cl}^-$  addition. In the presence of  $\text{Cl}^-$ , as shown in Fig. 3b and c, there was no obvious inhibitory effect on CA degradation in the  $\text{Co}^{2+}$ /PMS system with 20 mM TBA, while CA degradation decreased slightly as TBA increased to 1 M. This indicated  $\cdot\text{OH}$  was not the primary radical because it is difficult to form in an acidic solution (eqn (11)).<sup>34</sup> Besides, partial inhibitory on CA removal by adding 20 mM MeOH and complete inhibitory with 1 M MeOH were observed (see Fig. 3b), which suggested  $\text{SO}_4^{\cdot-}$  was the primary oxidant in the  $\text{Co}^{2+}$ /PMS system at low  $\text{Cl}^-$  concentration (1 mM). However, in the presence of 100 mM  $\text{Cl}^-$  (shown in Fig. 3c), only partially restrained on CA removal was detected by adding 1 M MeOH. That revealed  $\text{SO}_4^{\cdot-}$  was not the dominant oxidant in the presence of 100 mM  $\text{Cl}^-$ . Therefore,  $\text{SO}_4^{\cdot-}$  was the primary oxidant in the  $\text{Co}^{2+}$ /PMS system at low  $\text{Cl}^-$  levels ( $\leq 1 \text{ mM}$ ), whereas other reactive oxygen species might be predominant at high  $\text{Cl}^-$  concentrations.



### 3.4 Non-radical identification

The low solubility of  $\text{Co}^{3+}$  ( $k_{\text{sp}} = 1.6 \times 10^{-44}$ ) limits its presence in solutions at pH 3.0.<sup>17</sup> Hence, although  $\text{Co}^{3+}$  could exist in the  $\text{Co}^{2+}$ /PMS system, it contributes very little to CA oxidation.

Recent studies confirmed that high-valent cobalt-oxo [ $\text{Co}^{4+}$ ] species played a significant role in the oxidation of organic pollutants by  $\text{Co}^{2+}$ /PMS.<sup>16,17</sup> PMSO reacts readily with  $\text{Co}^{4+}$  to produce  $\text{PMSO}_2$ , though  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  cannot oxidize PMSO to  $\text{PMSO}_2$ .<sup>17</sup> Hence, the consumption of PMSO and formation of  $\text{PMSO}_2$  were conducted to identify the presence of  $\text{Co}^{4+}$ . As shown in Fig. 4a, PMSO directly oxidizes to  $\text{PMSO}_2$  with  $\eta$ -( $\text{PMSO}_2$ ) (represents the conversion ratio of PMSO to  $\text{PMSO}_2$ ) approaching 100% by PMS alone. For the PMS/ $\text{Cl}^-$  system, PMSO oxidation increased as the  $\text{Cl}^-$  increased from 1 to 100 mM, but formation of  $\text{PMSO}_2$  decreased in the co-presence of PMS and  $\text{Cl}^-$ . For example, the  $\eta$ -( $\text{PMSO}_2$ ) was 93.2% at 1 mM  $\text{Cl}^-$ , however, it was only 54.9% at  $[\text{Cl}^-]_0 = 100 \text{ mM}$ . Some reactive chlorine may have formed when  $\text{Cl}^-$  was 100 mM and oxidized PMSO to produce non- $\text{PMSO}_2$  products that lowered the  $\text{PMSO}_2$  formation rate. However, the loss rate of PMSO accelerated in the  $\text{Co}^{2+}$ /PMS/ $\text{Cl}^-$  system as compared to the PMS/ $\text{Cl}^-$  system (Fig. 4b). Additional consumption of PMSO after  $\text{Co}^{2+}$  addition suggested that other oxidants (e.g.,  $\text{Co}^{4+}$ ,  $\text{SO}_4^{\cdot-}$  or  $\cdot\text{OH}$ ) might transform PMSO. At the same time, the formation of  $\text{PMSO}_2$  was higher in the presence of  $\text{Co}^{2+}$  (Fig. 4b), which indicated formation of  $\text{Co}^{4+}$  and rapid oxidation of PMSO to  $\text{PMSO}_2$  (rate constant,  $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ). Additional consumption of PMSO was much higher than  $\text{PMSO}_2$  formation when  $\text{Co}^{2+}$  was involved (Fig. S5†), which confirmed that  $\text{Co}^{4+}$  was not the only reactive oxygen species responsible for PMSO oxidation. Moreover, Liu *et al.*<sup>17</sup> reported  $\text{Co}^{4+}$ ,  $\text{SO}_4^{\cdot-}$ , and  $\cdot\text{OH}$  existed in solution when the PMS/ $\text{Co}^{2+}$  ratio  $> 10$ . The PMS/ $\text{Co}^{2+}$  ratio in this study was 10 and our results agreed with those of Liu *et al.*<sup>17</sup>

As depicted in Fig. S6,† the effect of PMSO on CA degradation was investigated. CA degradation dropped significantly in the  $\text{Co}^{2+}$ /PMS system in the presence of both PMSO and  $\text{Cl}^-$ . This confirmed that PMSO may act as a scavenging agent for high-valent cobalt, PMS, and free radicals, which led to the inhibitory degradation of CA in the  $\text{Co}^{2+}$ /PMS system. For the PMS/ $\text{Cl}^-$  system, the degradation efficiency of CA reached 75.1% in 100 mM  $\text{Cl}^-$ , while complete inhibition of CA degradation with

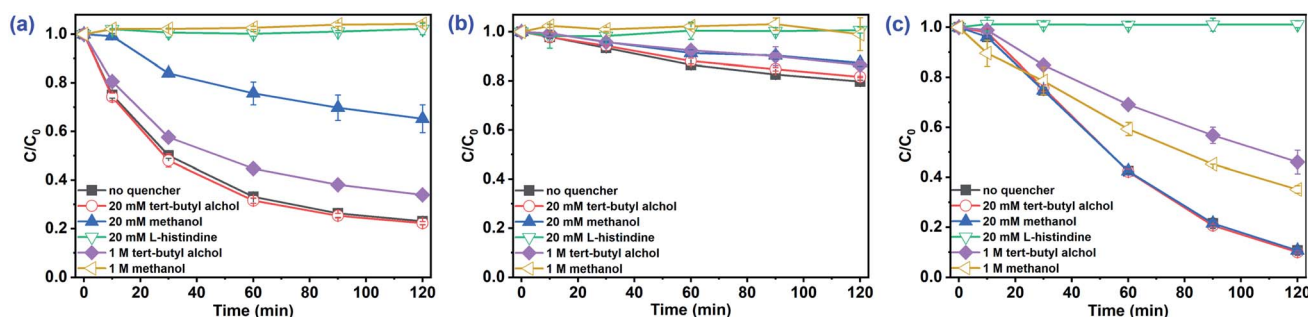


Fig. 3 Effect of radical scavengers on CA degradation in the  $\text{Co}^{2+}$ /PMS system. Experimental conditions:  $[\text{CA}]_0 = 0.1 \text{ mM}$ ,  $[\text{Co}^{2+}]_0 = 0.01 \text{ mM}$ ,  $[\text{PMS}]_0 = 0.5 \text{ mM}$ , pH 3.0, (a) 0 mM  $\text{Cl}^-$ ; (b) 1 mM  $\text{Cl}^-$ ; (c) 100 mM  $\text{Cl}^-$ .



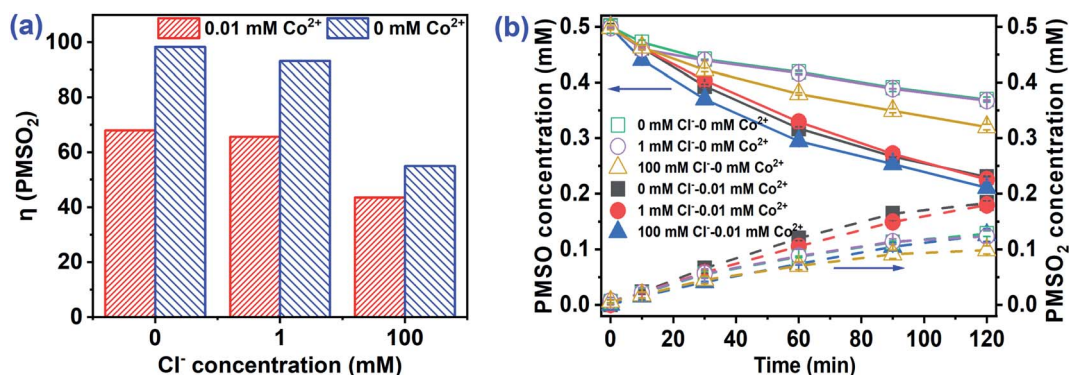


Fig. 4 (a)  $\eta(\text{PMSO}_2)$ , (b) PMSO loss and PMSO<sub>2</sub> corresponding production in  $\text{Co}^{2+}/\text{PMS}$  at different  $\text{Cl}^-$  concentrations. Experimental conditions:  $[\text{PMS}]_0 = 0.5 \text{ mM}$ ,  $[\text{PMSO}]_0 = 0.5 \text{ mM}$ , pH 3.0.

added PMSO. Chlorine species ( $\text{HOCl}/\text{Cl}_2$ ) generated by the reaction of  $\text{Cl}^-$  and PMS could preferentially oxidize PMSO rather than CA.

### 3.5 Kinetic modeling

These results revealed that multiple ROS, including  $\text{SO}_4^{\cdot-}$ ,  $\cdot\text{OH}$ , and  $\text{Co}^{4+}$ , were produced in the  $\text{Co}^{2+}/\text{PMS}$  system. Kinetic modeling helped understand the various reactive species and their contributions to the overall degradation (see equations Table S1†). Fig. S7† shows a typical kinetic plot with a fitting degree above 98.0%.

As depicted in Fig. 5a–c, three main reactive species ( $\text{SO}_4^{\cdot-}$ ,  $\cdot\text{OH}$ , and  $\text{Co}^{4+}$ ) may oxidize CA during  $\text{Co}^{2+}/\text{PMS}$  in the absence of  $\text{Cl}^-$ . The concentration of  $\text{SO}_4^{\cdot-}$  ( $\sim 10^{-6} \text{ M}$ ) was approximately nine and four times higher than  $\cdot\text{OH}$ , and  $\text{Co}^{4+}$ , respectively. Thus, the contribution of  $\text{SO}_4^{\cdot-}$  to CA oxidation reached 99.96%, while the contribution of  $\text{Co}^{4+}$  ( $\sim 0.03\%$ ) and  $\cdot\text{OH}$  ( $\sim 0.01\%$ ) were negligible (Fig. 6). This agreed with

quenching experiments and further revealed that  $\text{SO}_4^{\cdot-}$  plays a primary role in the  $\text{Co}^{2+}/\text{PMS}$  system without  $\text{Cl}^-$  addition.

A rapid adverse impact of  $\text{Cl}^-$  on the yield of  $\text{SO}_4^{\cdot-}$  should be related to the quenching reaction of  $\text{SO}_4^{\cdot-}$  by  $\text{Cl}^-$  with a high rate constant of  $2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (eqn (12)). As a result, the contribution of  $\text{SO}_4^{\cdot-}$  dropped significantly from 99.96% to 0.28% as  $\text{Cl}^-$  levels increased from 0 to 300 mM. Notably,  $\text{Cl}^-$  facilitated the formation of  $\cdot\text{OH}$  ( $\sim 10^{-13} \text{ M}$ ) at low  $\text{Cl}^-$  concentrations ( $\leq 1 \text{ mM}$ ), while the  $\cdot\text{OH}$  levels decreased with additional  $\text{Cl}^-$  (Fig. 5). Overall, the contribution of  $\cdot\text{OH}$  was small regardless of the amount of  $\text{Cl}^-$  present and agreed with quenching test results. It has been reported that  $\cdot\text{OH}$  level was relatively low under acidic conditions.<sup>35,42</sup> However, the  $\text{Co}^{4+}$  concentration was relatively stable ( $\sim 10^{-10} \text{ M}$ ) as the initial  $\text{Cl}^-$  level increased from 0 to 300 mM. Consequently, the contribution of  $\text{Co}^{4+}$  was less than 0.04%. This was likely due to its low reactivity with CA ( $k = 2.82 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ ) and the transformation of  $\text{Co}^{4+}$  to  $\text{SO}_4^{\cdot-}/\cdot\text{OH}$  when the molar ratio of  $\text{PMS}/\text{Co}^{2+}$  exceeded 10.

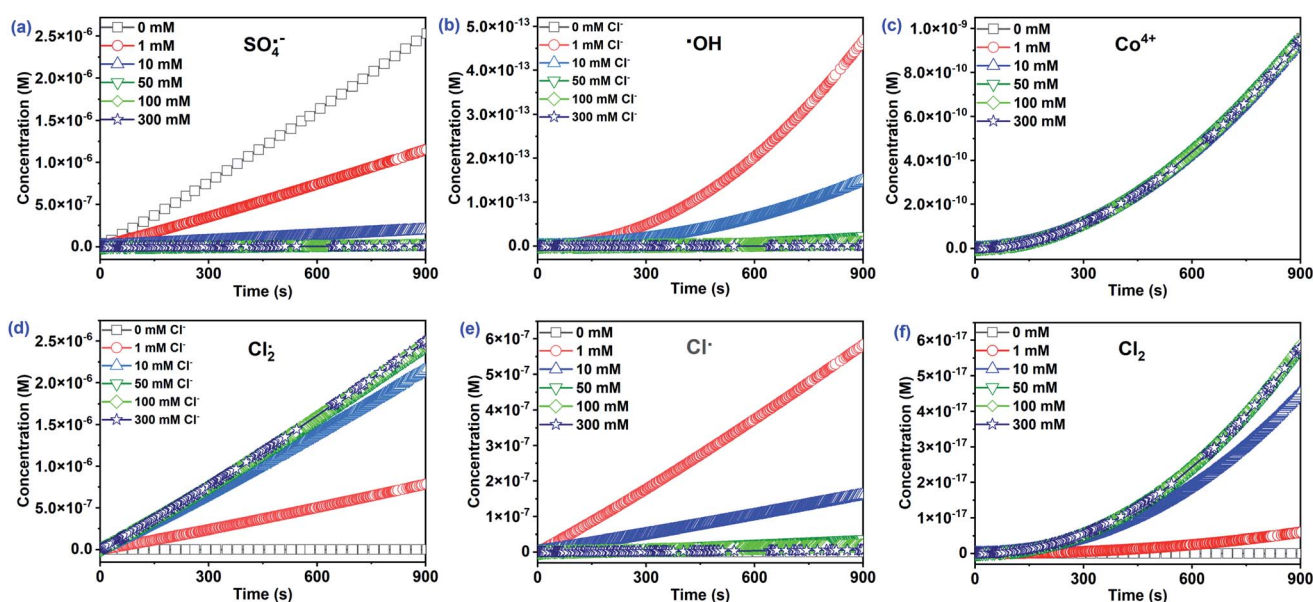
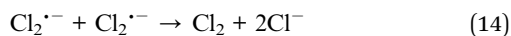
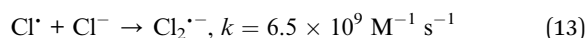
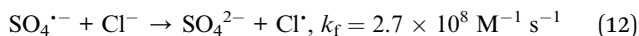


Fig. 5 The estimated concentration of primary reactive species at different  $\text{Cl}^-$  concentrations in the  $\text{Co}^{2+}/\text{PMS}/\text{Cl}^-$  system. Experimental conditions:  $[\text{CA}]_0 = 0.1 \text{ mM}$ ,  $[\text{Co}^{2+}]_0 = 0.01 \text{ mM}$ ,  $[\text{PMS}]_0 = 0.5 \text{ mM}$ , pH 3.0.



Interestingly, the  $\text{Cl}_2^{\cdot-}$  concentration was overwhelming ( $\sim 10^{-5} \text{ M}$ ) among all chlorine reactive species and significantly increased with  $\text{Cl}^-$ . As a result, the contribution of  $\text{Cl}_2^{\cdot-}$  to CA degradation reached 99.44% with 300 mM  $\text{Cl}^-$ . The absolute predominance of  $\text{Cl}_2^{\cdot-}$  was due to two things—the high rate constant of the reaction between CA and  $\text{Cl}_2^{\cdot-}$  ( $k = 1.41 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) played a significant role in CA oxidation. Secondly, the transformation of  $\text{Cl}^\cdot$  to  $\text{Cl}_2^{\cdot-}$  with a high rate constant of  $6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (eqn (13)) relates to the high concentration of  $\text{Cl}_2^{\cdot-}$ . Furthermore, generation of  $\text{Cl}^\cdot$  increased (0–1 mM) and then decreased (1–300 mM) with added  $\text{Cl}^-$ . In the presence of 1 mM  $\text{Cl}^-$ ,  $\text{Cl}^\cdot$  accounted for 23.16% of CA oxidation due to its high CA reactivity ( $k = 5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and high production ( $\sim 10^{-7} \text{ M}$ ).  $\text{Cl}_2$  concentration had a similar increase as  $\text{Cl}_2^{\cdot-}$ , due to the conversion of the  $\text{Cl}_2^{\cdot-}$  to  $\text{Cl}_2$  as shown in eqn (14). The other three reactive species, ( $\text{HOCl}$ ,  $\text{ClO}^\cdot$ , and  $\text{ClOH}^{\cdot-}$ ) at relatively low concentrations, initially increased, then decreased with added  $\text{Cl}^-$  (Fig. S8†). Consequently, their contributions to CA were relatively low and were neglected.  $\text{Cl}_2^{\cdot-}$  should be the dominant reactive species for CA oxidation at  $[\text{Cl}^-]_0 > 1 \text{ mM}$ , while  $\text{SO}_4^{\cdot-}$  played a critical role at low  $\text{Cl}^-$  concentrations ( $\leq 1 \text{ mM}$ ) in the  $\text{Co}^{2+}/\text{PMS}$  system.

### 3.6 Mechanism and pathways

GC-MS analyzed the CA intermediates. The primary chlorinated by-products at different  $\text{Cl}^-$  concentrations (*i.e.*, 0, 1, and 100 mM) at 30 and 120 min are shown in Table S2.† The chlorinated

by-products increased with added  $\text{Cl}^-$  or reaction times. For example, 11 kinds of chlorinated by-products were detected in the  $\text{Co}^{2+}/\text{PMS}$  system without  $\text{Cl}^-$  addition, whereas 22 and 23 refractory chlorinated by-products at 1 mM and 100 mM  $\text{Cl}^-$  were detected, respectively (Table S2†). Based on the identified products and previous studies,<sup>9,43</sup> possible mechanisms and a CA degradation pathway were proposed (Fig. 7).

In the absence of  $\text{Cl}^-$ ,  $\text{SO}_4^{\cdot-}$  was the main reactive species in CA degradation. Thus, CA oxidation could proceed by three different pathways, including C1–O bond breaking, dechlorination, and attack on the C7 position of CA. Firstly, cleavage of the C1–O bond formed 4-chlorophenol (**P1**). Dechlorination of 4-chlorophenol attacked by  $\text{SO}_4^{\cdot-}$  may generate phenol (not detected, which implied in the present study) and the release of chloride ions (shown in Scheme 1a).<sup>44</sup> Interestingly, chloride ions undergo oxidation by  $\text{SO}_4^{\cdot-}$  to produce chlorine radicals that form chlorinated aromatic by-products (**P2** and **P3**) by nucleophilic addition. Peng *et al.*<sup>36</sup> also indicated chlorine atoms of chlorinated azo dyes might be partially released as inorganic ions, which undergo subsequent rechlorination. Alternatively,  $\text{SO}_4^{\cdot-}$  initially reacts with CA, which led to CA dechlorination, followed by oxidation of the intermediate by  $\text{SO}_4^{\cdot-}$  to generate chlorinated by-products (**P4**). In the last way, the C7 position of CA was attacked by  $\text{SO}_4^{\cdot-}$  followed by demethylation and decarboxylation intermediates, such as 2-(4-chloro-phenoxy)-propionic acid (not detected) and acetic acid-4-chlorophenyl ester (**P5**), which was further transformed to chlorinated by-products (**P6** and **P7**) through chlorination, respectively. Furthermore, the aromatic ring was gradually cleaved to produce organic acid compounds such as butanedioic acid (**P8**), methacrylic acid (**P9**), and glycolic acid (**P10**). Finally, short-chain alcohol compounds (*e.g.*, glycerol (**P11**) and ethylene glycol (**P12**)) formed and eventually oxidized into  $\text{CO}_2$ .

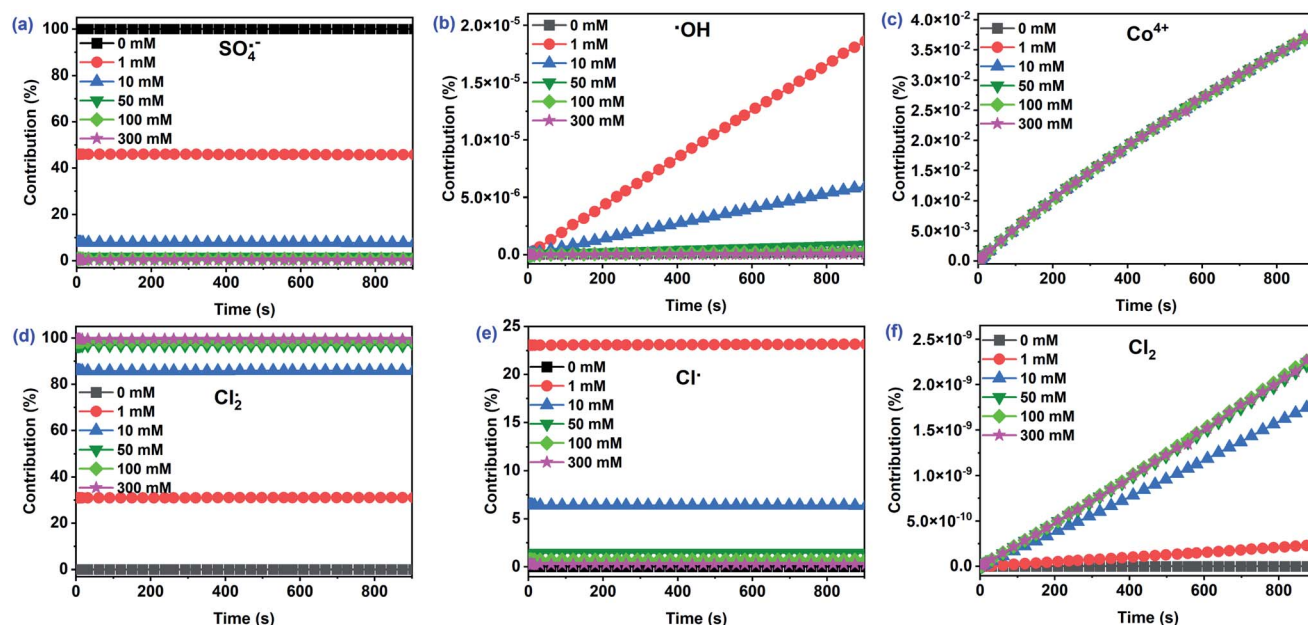


Fig. 6 The contribution of primary reactive species to CA degradation at different  $\text{Cl}^-$  concentrations in the  $\text{Co}^{2+}/\text{PMS}/\text{Cl}^-$  system. Experimental conditions:  $[\text{CA}]_0 = 0.1 \text{ mM}$ ,  $[\text{Co}^{2+}]_0 = 0.01 \text{ mM}$ ,  $[\text{PMS}]_0 = 0.5 \text{ mM}$ , pH 3.0.





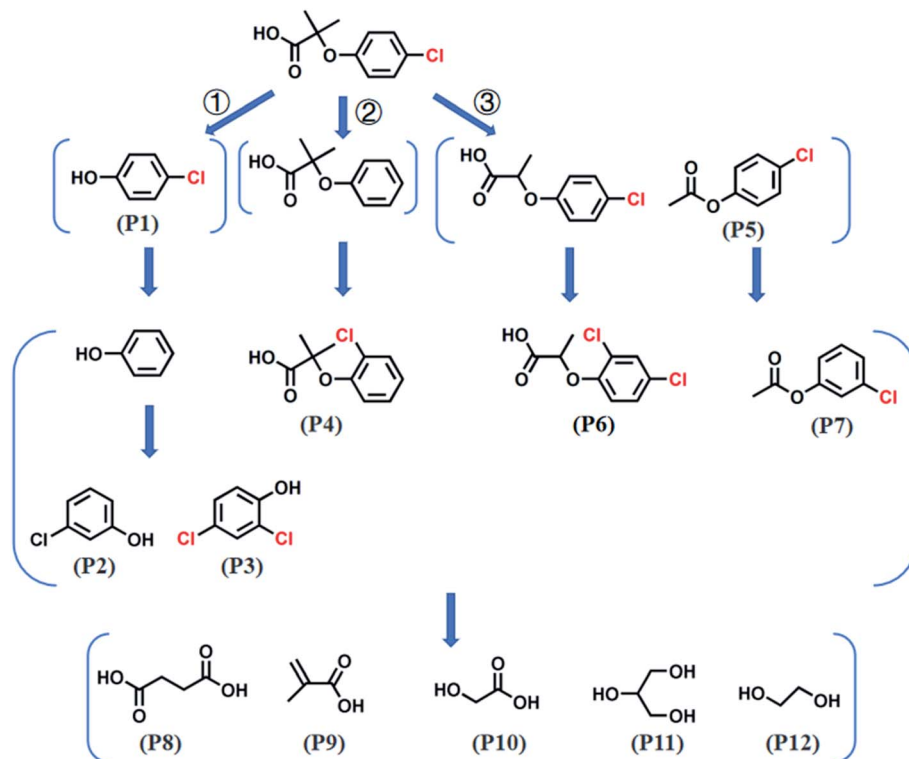
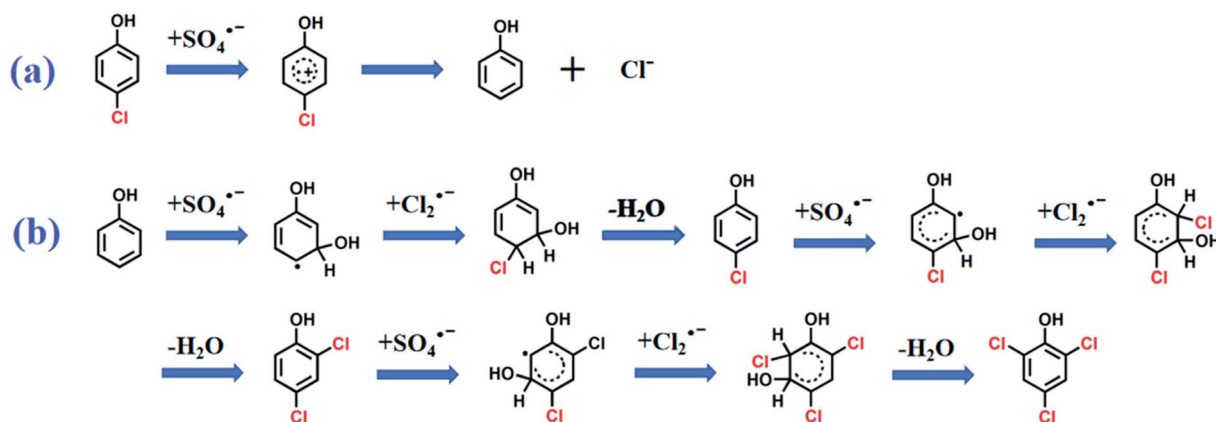


Fig. 7 A possible CA oxidation pathway in the  $\text{Co}^{2+}$ /PMS system. Experimental conditions:  $[\text{CA}]_0 = 0.1 \text{ mM}$ ,  $[\text{Co}^{2+}]_0 = 0.01 \text{ mM}$ ,  $[\text{PMS}]_0 = 0.5 \text{ mM}$ , pH 3.0.

and  $\text{H}_2\text{O}$ . The identification of polychlorinated by-products (**P2**, **P3**, and **P6**) during CA removal without exogenous  $\text{Cl}^-$  addition provided direct evidence for dechlorination and rechlorination of endogenous  $\text{Cl}^-$ . Furthermore, the formation of various chlorinated by-products also explains the high degradation efficiency (81.0%) but low mineralization rate (9.15%) within 120 min during CA removal in the absence of  $\text{Cl}^-$ .

In the presence of  $\text{Cl}^-$ ,  $\text{SO}_4^{\bullet-}$  was scavenged by  $\text{Cl}^-$  to produce less reactive chlorine radicals ( $\text{Cl}^\bullet/\text{Cl}_2^{\bullet-}$ ), which resulted in the reduction of CA oxidation. The inhibition of  $\text{Cl}^-$  is vital at low chloride levels ( $\leq 1 \text{ mM}$ ). Additional  $\text{Cl}^-$  dramatically enhanced CA oxidation, whereas the overall degradation rate

was still lower than in the absence of  $\text{Cl}^-$ . Hence,  $\text{Cl}_2^{\bullet-}$  was the dominant chlorine species contributing to CA degradation under chloride-rich conditions. More refractory polychlorinated by-products (chlorine atom number  $\geq 2$ ) were produced with additional  $\text{Cl}^-$ , such as 3,4-dichlorophenol, 2,3-dichlorophenol, and 2,5-dichlorophenol. Thus, the mineralization rate dropped as the  $\text{Cl}^-$  concentration increased. The oxidation pathways of CA involving  $\text{Cl}^-$  might include C1–O bond cleavage, chlorination, dechlorination, and rechlorination process. Notably, 2,4,6-trichlorophenol was generated as the chlorinated by-product of CA in the presence of exogenous  $\text{Cl}^-$ . It was assumed that chlorination phenol was initiated by  $\text{Cl}_2^{\bullet-}$  attack of the



Scheme 1 The possible pathway of (a) dechlorination and (b) chlorination on CA degradation intermediates.



degradation product radicals, yielding 2,4,6-trichlorophenol (Scheme 1b). This result further proved that a higher exogenous  $\text{Cl}^-$  concentration produced additional chlorine radicals, and then oxidized CA to produce more chlorinated by-products, consistent with previous reports.<sup>25,31</sup>

## 4 Conclusions

The degradation kinetics and mechanism of CA were studied in the  $\text{Co}^{2+}$ /PMS system. The reaction rates of CA increased with added  $\text{Co}^{2+}$  and PMS though varied slightly with initial pH. Furthermore,  $\text{Cl}^-$  had a dual effect (inhibitory then promoting) on CA degradation. Intermediate identification by GC-MS revealed that more refractory polychlorinated by-products (chlorine atom number  $\geq 2$ ) were produced in the  $\text{Co}^{2+}$ /PMS/ $\text{Cl}^-$  system, which resulted in a decreased CA mineralization rate. According to quenching experiments and kinetic modeling,  $\text{SO}_4^{\cdot-}$  (45.7%) played the main role in CA degradation, followed by  $\text{Cl}_2^{\cdot-}$  (31.1%) and  $\text{Cl}^{\cdot}$  (23.2%) at low  $\text{Cl}^-$  levels ( $\leq 1$  mM), whereas  $\text{Cl}_2^{\cdot-}$  was the predominant radical when  $[\text{Cl}^-]_0 > 1$  mM. However, the contribution of  $\text{Co}^{4+}$  to CA degradation was relatively low regardless of added  $\text{Cl}^-$ . A possible CA degradation pathway in saline wastewater was proposed, including cleavage of the C1-O bond, chlorination, dechlorination, and rechlorination process. Our findings indicated the introduction of exogenic  $\text{Cl}^-$  increased the difficulty in oxidative degradation of CA. Hence, it is imperative to explore other effective technologies for CA treatment in saline wastewater.

## Conflicts of interest

There are no conflicts to declare.

## Author contributions

Jiale Wang: Conceptualization, Visualization, Writing-original draft, Data curation. Siyi Fan: Data curation, Resources, Data curation. Zhirui Xu: Resources, Validation. Jiaqi Gao: Investigation, Resources. Ying Huang: Conceptualization, Funding acquisition, Software, Writing-review & editing, Supervision. Xubiao Yu: Methodology, Funding acquisition, Supervision. Huihui Gan: Visualization, Investigation, Funding acquisition.

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