

Kinetics of Inhibition of Dichlorophenol Oxidation by NaCl over Fe-Cu-Pillared Clay

Shiwei Zhou¹; Jingzhe He²; and Xiaoli Bi³

Abstract: Catalytic wet peroxide oxidation (CWPO) of dichlorophenols (DCPs) over Fe-Cu-pillared clay (PILC) without and with NaCl was investigated. Concentration change dynamics in H₂O₂, Cl⁻, and hydroxyl radicals (·OH) during DCP oxidation were also studied. Additionally, the intermediates formed were detected by liquid chromatography-mass spectroscopy (LC-MS). The results showed that the presence of NaCl inhibited the DCP oxidation rate to some extent, where induction time (T_I) was lengthened from 75.9 to 93.6 min, and half-decomposition time ($T_{1/2}$) was extended to 20.6 min (from 86.6 to 107.2 min) as compared with control (without NaCl addition). However, NaCl only strongly inhibited the oxidation rate of ortho-substituted DCPs such as 2,6-DCP, where T_I was lengthened to 80 min (from 290.7 to 370.4 min), but not meta-DCPs or para-DCPs. Further investigation showed that NaCl did not affect the conversion (dechlorination and hydroxylation) of DCPs and also did not change the DCP oxidation path. It was hypothesized that the inhibitory mechanism of NaCl on ortho-DCP oxidation was mainly due to inhibiting the rate-limiting step of H₂O₂ decomposition (lengthening the induction period from 350 to 510 min) by competing with H₂O₂ for the complexation of Fe (III), secondary due to scavenging of ·OH (about 21%) to form chlorine radicals such as ·Cl₂. DOI: 10.1061/(ASCE)EE.1943-7870.0001550. © 2019 American Society of Civil Engineers.

Author keywords: Dichlorophenol (DCP); Fenton-like reaction; Fe-Cu-pillared clay (Fe-Cu-PILC); Sodium chloride (NaCl); Induction time (T_I); Hydroxyl radical (·OH).

Introduction

Chlorophenols (CPs) are ubiquitous in wastewaters, soils, and sediments, and most of them are listed as priority toxic pollutants due to their high toxicity and hard biodegradability (Pera-Titus et al. 2004). Thus, the development of efficient methods for CP removal is becoming an important field of study. In the last few years, catalytic wet peroxide oxidation (CWPO) technology for the abatement of CP-bearing wastewater using Al-Fe-pillared or Al-Cu-pillared clays (PILCs) under very mild conditions (room temperature and atmospheric pressure) has been shown to be successful (Catrinescu et al. 2011, 2012; Galeano et al. 2014; Zhou et al. 2014; Nidheesh 2015; Butthiyappan et al. 2016; Baloyi et al. 2018). The reactivity of these heterogeneous catalysts has been investigated and reaction conditions such as initial CP concentration, H₂O₂ concentration and catalyst dosage, solution pH, and reaction temperature have also been examined (Table 1). However, there are still significant knowledge gaps in understanding the kinetic process and interaction mechanism of this complicated Fenton-like reaction. Little information in literature is available and is somewhat conflictive. For example, some researchers have considered that the existing chloride ions during the CP oxidation process strongly inhibit the abatement efficiency of pollutants because of scavenging the

transitory hydroxyl radicals (·OH) or competing with H₂O₂ for the complexation of Fe (III) (De Laat et al. 2004; De Laat and Le 2006; Pignatello et al. 2006; Lin et al. 2015). Even the inhibitory effect was noticeable at Cl⁻ concentrations higher than 0.01 M (Pignatello et al. 2006; Machulek et al. 2007). By contrast, some studies have found that the presence of chloride ions significantly increased the oxidation rate of nonbiodegradable pollutants (Vione et al. 2005; Mahamuni and Pandit 2006; Micó et al. 2013; Zhou et al. 2016), which was attributed to the salting-out effect, the participation of ·Cl in the reaction, or the formation of chlorinated intermediates that acted as electron shuttles.

Some amounts of chloride atom would release into solution by dechlorination of CPs, generating chloride ions. Additionally, inorganic anions, especially Cl⁻, were usually detected in polluted environments. Thus, the effect of chloride ions on CP oxidation kinetics should be demonstrated in detail. There was different reactivity for different CPs with different positions of chloride atoms due to the σ -electron withdrawing conductive effect, π -electron donating conjugative effect, and steric hindrance effect of chlorine (Tang and Huang 1995; Leyva et al. 2003; Zhang et al. 2003; Zhou et al. 2011). It was speculated that Cl⁻ might exhibit different inhibitory effects on the oxidation rate of CPs with different substituent positions of chlorine on the phenyl ring. In this work, therefore, the reaction kinetics of CWPO of dichlorophenols (DCPs) with and without NaCl addition was investigated, and the aim was to find evidence of the significant inhibition of ortho-substituted CP oxidation by chloride ion.

Materials and Methods

Fe-Cu-PILC Catalyst

Using a common copolymerization procedure, a Fe-Cu-PILC was synthesized in a previous study (Zhou et al. 2014) and characterized by field emission scanning electron microscope with an

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Table 1. Brief summary of the catalytic wet peroxide oxidation of chlorophenols over clay-based catalysts

Clay catalyst	Chlorophenol	Operation conditions	Best performances	Reference
Cu(II)-kaolinite (C1), Cu(II)-montmorillonite (C2)	2-CP, 4-CP, 2,4-DCP	[CP] = 0.2–1.0 mM, $n(\text{H}_2\text{O}_2)/n(\text{CP}) = 1-10$, [C1] = 0.4–2.0 g/L, [C2] = 0.1–0.5 g/L, $T = 333-353$ K, $t = 5-480$ min, pH = 2–7	$n(\text{H}_2\text{O}_2)/n(\text{CP}) = 10$, [C1] = 1.2 g/L, [C2] = 0.5 g/L, $T = 333$ K, $t = 480$ min, no pH adjustment	Khanikar and Bhattacharyya (2013)
Iron oxide-pillared montmorillonite	2,3-DCP	[DCP] = 100 mg/L, $[\text{H}_2\text{O}_2] = 30,150,300$ mg/L, [catalyst] = 1 g/L, $T = 25^\circ\text{C}$, $t = 3.5$ h	[DCP] = 100 mg/L, $[\text{H}_2\text{O}_2] = 150$ mg/L, $n(\text{H}_2\text{O}_2)/n(\text{DCP}) = 7$, [catalyst] = 1 g/L, $T = 25^\circ\text{C}$, $t = 3.5$ h	Virkute and Varma (2014)
Fe-Mt, Fe-(Al-PILC), (Al-Fe)-PILC	4-CP	[4-CP] = 100–2000 mg/L, $[\text{H}_2\text{O}_2] = 0.15-0.6$ M, $T = 30-90^\circ\text{C}$, pH = 3.5–6.0	[4-CP] = 312 mg/L, $[\text{H}_2\text{O}_2] = 0.3$ M, [catalyst] = 5 g/L, $T = 70^\circ\text{C}$, $t = 240$ min, pH = 3.5	Catrinescu and Teodosiu (2007)
Al-Fe PILC	4-CP		[4-CP] = 155.6 $\mu\text{mol/L}$, $n(\text{H}_2\text{O}_2)/n(4\text{-CP}) = 13.5$, [catalyst] = 0.5 g/L, pH = 3.5, $T = 30^\circ\text{C}$, $t = 100-150$ min (VIS or UV), $t = 250$ min (Dark)	Catrinescu et al. (2012)
Cu-Al hydrotalcite/clay composite	2-CP, 3-CP, 4-CP, 3,5-DCP, 3,4-DCP, 2,5-DCP, 2,4-DCP, 2,6-DCP	[CP] = 2.0 mM, $n(\text{H}_2\text{O}_2)/n(\text{CP}) = 10-25$, [catalyst] = 0.5–2.5 g/L, $T = 30-50^\circ\text{C}$, $t = 60-300$ min, pH = 2.8–7.9	$n(\text{H}_2\text{O}_2)/n(4\text{-CP}) = 13.5$, [catalyst] = 0.5 g/L, pH = 3.5, $T = 30^\circ\text{C}$, $t = 100-150$ min (VIS or UV), $t = 250$ min (Dark)	Zhou et al. (2011)
Mn(II)-MCM41	2-CP, 2,4-DCP, 2,4,6-TCP	[CP] = 0.2–1.2 mM, $n(\text{H}_2\text{O}_2)/n(\text{CP}) = 1-20$, [catalyst] = 2–10 g/L, $T = 333-413$ K, $t = 300$ min, pH 3–9	$n(\text{H}_2\text{O}_2)/n(\text{CP}) = 10$, [catalyst] = 2 g/L, $T = 353$ K, $t = 300$ min, no pH adjustment	Chalitha and Bhattacharyya (2008)
$\text{Fe}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$	4-CP, 2,4-DCP, 2,4,6-TCP	[CP] = 100 mg/L, $[\text{H}_2\text{O}_2]$ at stoichiometric dose, [catalyst] = 1 g/L, $T = 50-90^\circ\text{C}$, $t = 240$ min, pH = 3	[CP] = 100 mg/L, $[\text{H}_2\text{O}_2]$ at stoichiometric dose, [catalyst] = 1 g/L, $T = 50^\circ\text{C}$, $t = 240$ min, pH = 3	Munoz et al. (2013)
Chromium-zinc ferrite nanocomposites	4-CP, 2,4-DCP	[CP] = 0.75–1.75 g/L, $n(\text{H}_2\text{O}_2)/n(\text{CP}) = 12-18$, [catalyst] = 0.3–1.0 g/L, $T = 298-343$ K	[catalyst] = 0.5 g/L, $n(\text{H}_2\text{O}_2)/n(4\text{-CP}) = 13$, [4-CP] = 1 g/L, $T = 298$ K, $t = 60$ min, pH = 6.2–6.9; $n(\text{H}_2\text{O}_2)/n(2,4\text{-DCP}) = 12$, [2,4-DCP] = 1 g/L, $T = 343$ K, $t = 75$ min, pH = 5.2–7.03	Nair and Kurian (2018)

Table 2. Characterization of Fe-Cu-PILC catalyst

Material	d_{001} (nm)	SSA ($\text{m}^2 \text{g}^{-1}$)	Elemental composition (% by wt.)								
			O	Si	Al	Na	Mg	Fe	Cu	Cl	Total
Na ⁺ -bentonite	1.15	21	57.4	27.4	10.0	1.8	1.5	1.9			100.0
Fe-Cu-PILC	1.57	136	61.8	17.1	13.7		1.0	4.4	1.3	0.8	100.1

Source: Data from Zhou et al. (2014).

energy-dispersive X-ray spectroscopy (FE-SEM-EDX), powder X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR), thermogravimetric analysis (TGA), and specific surface area (SSA) (Table 2). It exhibited high catalytic activity and high stability, in which 100% of 4-CP and 63% of total organic carbon (TOC) conversion were achieved within 2 h at 40°C, showing a low amount of active metal leaching (Fe = 6.7% and Cu = 9.2%) (Zhou et al. 2014). Therefore, it was used in this work as a high-efficiency heterogeneous catalyst.

Chemical Regents

DCPs (2,3-DCP, 2,4-DCP, 2,5-DCP, 2,6-DCP, 3,4-DCP, and 3,5-DCP) with a minimum purity of 95% were purchased from Alfa Aesar (Tianjin, China). The other analytical reagents, such as H₂O₂ (30 wt.%), ammonium metavanadate, and methylene blue, were purchased from Sinopham Chemical Reagent Co., Shanghai, China. Ultrapure water (18.2 MΩ cm, Pall, New York) was used in the experiments.

Catalytic Oxidation of DCPs by H₂O₂ under Presence and Absence of NaCl

Following the method described in the previous studies (Zhou et al. 2011, 2014), the catalytic oxidation reaction was carried out in a 500-mL three-necked glass flask fitted with a reflux condenser, magnetic stirrer, and thermostated water bath. For a typical run, 250 mL of DCPs (2 mM) and 0.25 g of catalyst in powder form and 0.25 g of NaCl were loaded into the flask. After the reaction mixture was magnetically stirred and heated to 40°C, H₂O₂ (10 mmol) was added at once, which initiated the reaction. During all the oxidation reactions, 10-mL aliquots were withdrawn at selected time intervals and filtered by means of 0.22-μm membranes to analyze DCPs and their intermediates, Cl⁻, OH, and H₂O₂.

Analytical Methods

The concentration of DCPs was determined by high-performance liquid chromatography (HPLC) equipped with a diode array detector (DAD) and a C-18 reversed-phase column (5 μm, 4.6 × 150 mm) (Agilent 1260, Agilent Technologies, Santa Clara, California), using mobile phase (methanol:water = 80:20) and a UV detector operating at 284 nm (Lv et al. 2016). The injection volume was 5 μL and the mobile phase flow rate was 1 mL min⁻¹ at 25°C.

In order to clarify the oxidation pathway of DCPs, we monitored the appearance of the intermediate compounds by an Agilent 1260 liquid chromatograph and an Agilent 5975C mass spectrometer (HPLC/MS) equipped with a quartz capillary column (0.25 μm, 50 × 0.25 mm). The MS was worked at electron impact (EI) at 70 eV, ion source temperature at 200°C, and injection temperature at 280°C.

Cl⁻ was detected by ion chromatography (DX-100, Dionex, Germany). H₂O₂ was analyzed by UV-Vis spectrophotometer (UV-1200, Shimadzu Co., Japan) based on the formation of red-orange color peroxovanadium cation after the reaction of H₂O₂ with NH₄VO₃ in acidic medium (Nogueira et al. 2005). According to

the method of methylene blue dye test (Satoh et al. 2007), formed OH during CWPO of DCPs with and without NaCl was also quantified by UV-1200 at 660 nm.

Kinetic Model of DCP Oxidation

The Fenton-like reaction of CPs showed an induction period followed by a rapid oxidation, yielding an S-shaped profile of concentration versus time (Catrinescu et al. 2012; Zhou et al. 2014). A kinetic model based on Fermi's function can be used to describe the reaction process:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp[k(t - t_*)]} \quad (1)$$

where k = equivalent apparent first-order rate constant (min⁻¹); and t_* = transition time (min), that is, half-disappearance time ($T_{1/2}$) (Herney-Ramirez et al. 2011; Silva et al. 2012; Rache et al. 2014; Zhou et al. 2014; Minz et al. 2018).

Further, the induction time (T_I), which could be determined by setting the third differential of the model equal to zero (Luo et al. 2009), was calculated as follows (Zhou et al. 2014):

$$T_I = t_* + \frac{\ln(2 - \sqrt{3})}{k} \quad (2)$$

Data Quality Control and Statistical Analysis

The concentration was calculated by comparing the peak area (DCPs and Cl⁻) or absorbance (H₂O₂ and ·OH) of reaction solution with that of the standard curves, which were formulated according to straight-line equations, with $R^2 \geq 0.999$.

For each reaction, three repetitions were done. Average values and standard errors (SEs) were calculated using Microsoft Office Excel 2010; graphics and associated curve fitting were conducted with SigmaPlot for Windows version 12.0.

Results and Discussion

Chloride Ion Inhibits the Oxidation of DCPs

The oxidation data of DCPs by H₂O₂ over Fe-Cu-PILC fitted well Fermi's kinetic model described previously, with $R^2 = 0.9888$ – 0.9993 and $p \leq 0.0001$ (Fig. 1). The calculated parameters (k , $T_{1/2}$, and T_I) are listed in Table 3. Compared to control (without NaCl addition), after addition of NaCl, the oxidation of DCPs was inhibited to some extent, as shown in Fig. 1 and Table 3, where $T_{1/2}$ and T_I in the absence of NaCl were 86.6 (14.3–309.6 min) and 75.9 min (6.2–290.7 min), respectively, whereas in the presence of NaCl, they were 107.2 (15.4–412.3 min) and 93.6 min (10.3–370.4 min), respectively. Correspondingly, the average oxidation rate decreased from 0.0357 (0.00528–0.0767 mM min⁻¹) to 0.0341 mM min⁻¹ (0.00355–0.0762 mM min⁻¹). Further, k slightly increased from 0.180 (0.0671–0.395 min⁻¹) to 0.183 min⁻¹ (0.0314–0.434 min⁻¹). This means that there was an insignificant difference

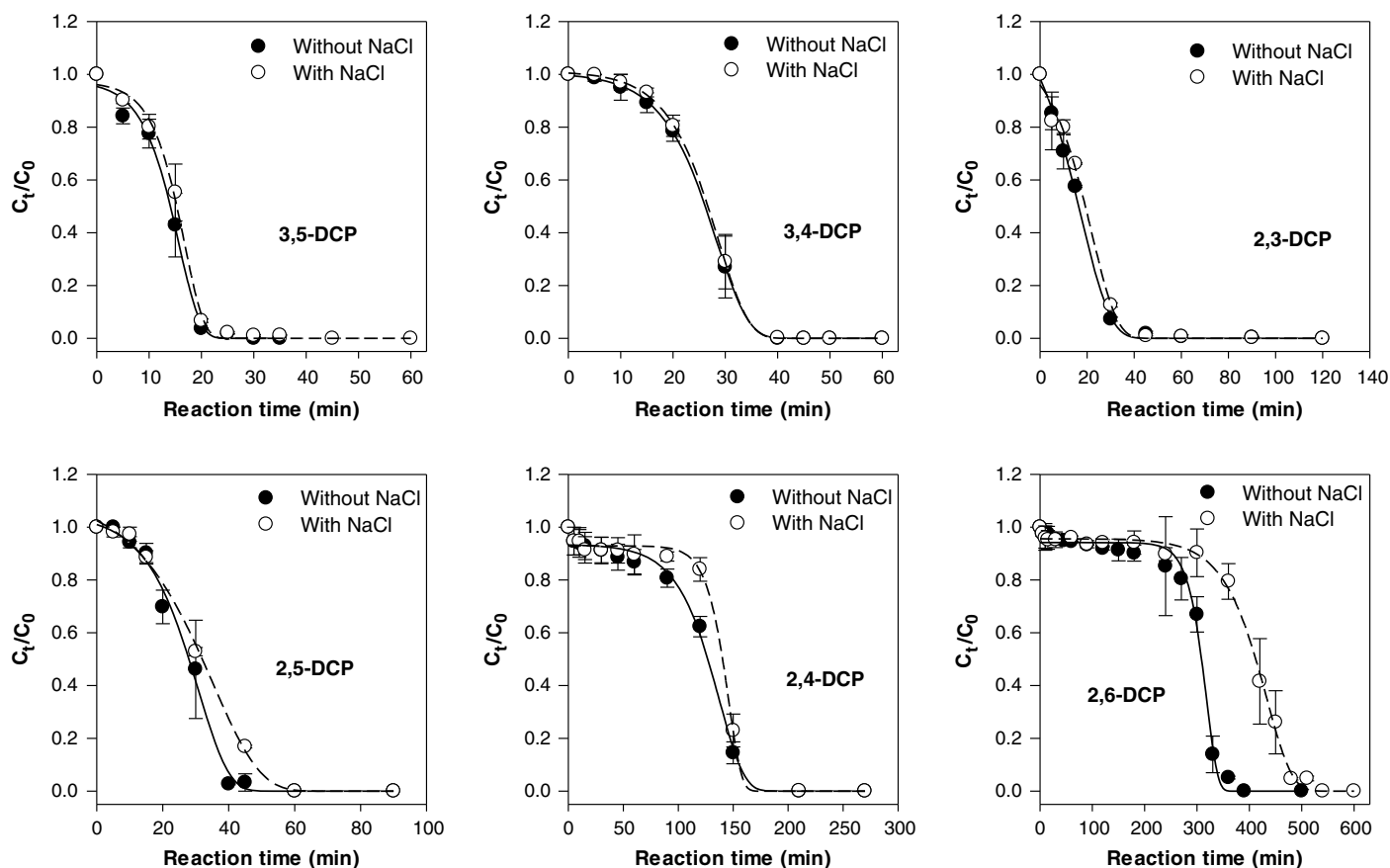


Fig. 1. Oxidation kinetics of DCPs without and with NaCl over Fe-Cu-PILC (reaction conditions: [DCP] = 2 mM; [H₂O₂] = 40 mM; [catalyst] = 1 g L⁻¹; [NaCl] = 1 g L⁻¹; and temperature of 40°C).

Table 3. Calculated values of rate constant (k) and half-disappearance time ($T_{1/2}$) obtained for the catalytic oxidation of DCPs

DCP	$T_{1/2}$ (min)		T_1 (min)		k (min ⁻¹)		Average rate (mM min ⁻¹)	
	Without NaCl	With NaCl	Without NaCl	With NaCl	Without NaCl	With NaCl	Without NaCl	With NaCl
3,5-DCP	14.3	15.4	10.9	12.4	0.395	0.434	0.0767	0.0762
3,4-DCP	25.6	26.1	20.0	20.6	0.234	0.241	0.0438	0.0438
2,3-DCP	15.0	18.6	6.2	10.3	0.150	0.159	0.0427	0.0414
2,5-DCP	27.0	30.6	18.9	19.7	0.164	0.121	0.0359	0.0286
2,4-DCP	128.3	140.0	108.6	128.1	0.0671	0.111	0.0101	0.0109
2,6-DCP	309.6	412.3	290.7	370.4	0.0696	0.0314	0.00528	0.00355

in the oxidation rate of DCPs without and with NaCl, and the inhibitory effect of NaCl on DCP oxidation was mainly ascribed to prolonging of induction time (T_1). From Fig. 1 and Table 3, it may be noted that only the oxidation rate of ortho-substituted DCPs was strongly inhibited by NaCl but not that of meta-DCPs or para-DCPs. For example, during the oxidation of 2,6-DCP with NaCl, T_1 was prolonged from 290.7 to 370.4 min; correspondingly, k and the average rate were decreased from 0.0696 to 0.0314 min⁻¹ and 0.00528 to 0.00355 mM min⁻¹, respectively. However, for the oxidation of 3,5-DCP and 3,4-DCP without and with NaCl, T_1 and the average rate did not apparently change (on average, 15.5 and 16.5 min and 0.06 and 0.06 mM min⁻¹, respectively).

Previous researchers illustrated that the inhibitory effect of NaCl was derived from chloride ions that effectively scavenged ·OH or competitively complexed with Fe (III) (De Laet et al. 2004; De Laet and Le 2006; Pignatello et al. 2006; Machulek et al. 2007; Lin et al. 2015). Thus, it could be concluded that Cl⁻ strongly inhibited

the oxidation rate of ortho-DCPs but not that of meta-DCPs or para-DCPs.

Inhibition Mechanism of Chloride Ions on Ortho-DCP Oxidation

In order to clarify the inhibition mechanism of chloride ions on DCP oxidation, the relationships among H₂O₂ decomposition, ·OH generation, dechlorination (Cl⁻ release), and oxidation of 3,4-DCP and 2,6-DCP without and with NaCl were investigated in detail (Figs. 2–4). It was found that shorter induction time (about 25 min) and a higher amount of decomposition (about 55%) occurred for H₂O₂ decomposition during 3,4-DCP oxidation (Fig. 2); correspondingly, more ·OH (about 2.8 μmol L⁻¹) was generated (Fig. 3). On the contrary, longer induction (about 350 min) and a lower amount of H₂O₂ decomposition (about 40%) and less ·OH formation (about 1.5 μmol L⁻¹) were observed for that during

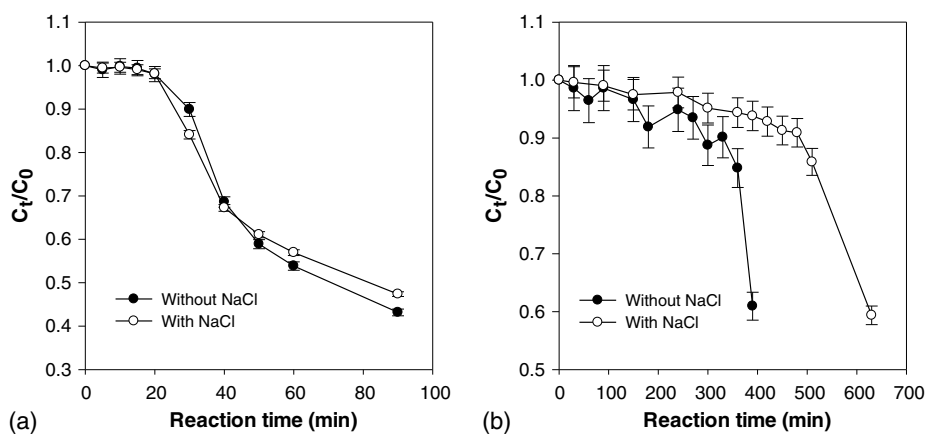


Fig. 2. Kinetics of H_2O_2 decomposition during catalytic reaction of (a) 3,4-DCP; and (b) 2,6-DCP without and with NaCl over Fe-Cu-PILC (reaction conditions: $[DCP] = 2 \text{ mM}$; $[H_2O_2] = 40 \text{ mM}$; $[catalyst] = 1 \text{ g L}^{-1}$; $[NaCl] = 1 \text{ g L}^{-1}$; and temperature of 40°C).

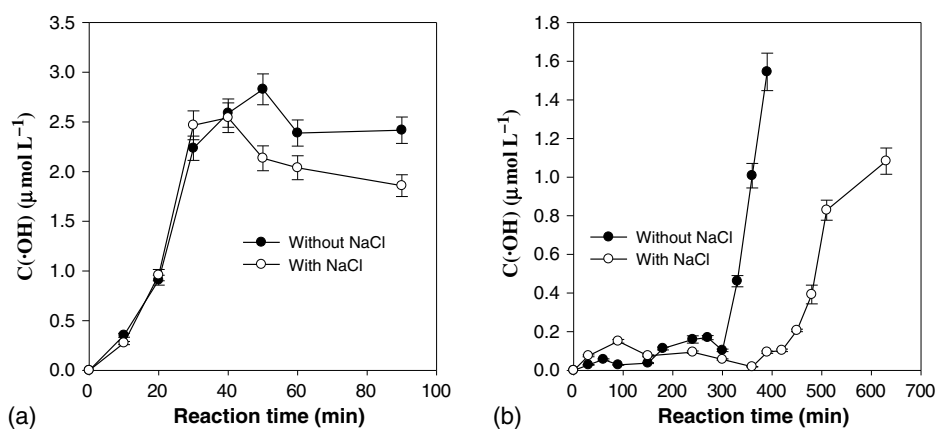


Fig. 3. Kinetics of $\cdot\text{OH}$ formation during catalytic reaction of (a) 3,4-DCP; and (b) 2,6-DCP without and with NaCl over Fe-Cu-PILC (reaction conditions: $[DCP] = 2 \text{ mM}$; $[H_2O_2] = 40 \text{ mM}$; $[catalyst] = 1 \text{ g L}^{-1}$; $[NaCl] = 1 \text{ g L}^{-1}$; and temperature of 40°C).

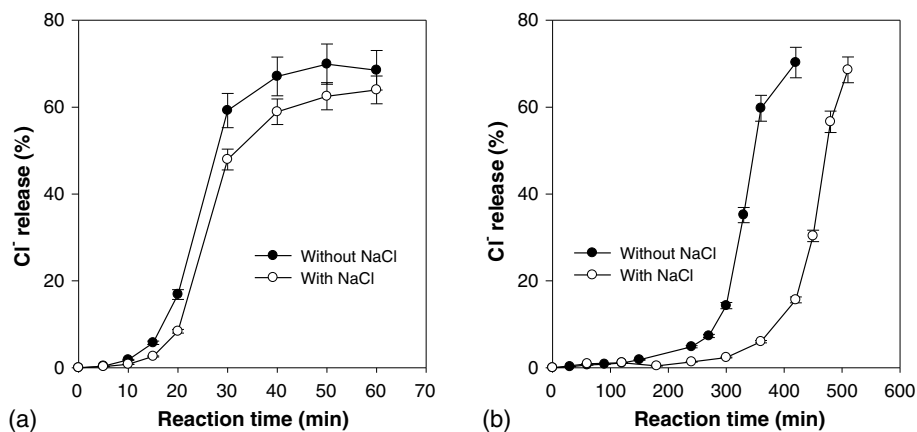
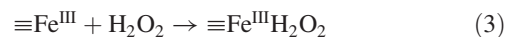
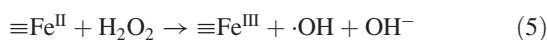
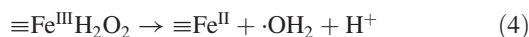


Fig. 4. Kinetics of dechlorination (Cl^- release) during catalytic oxidation of (a) 3,4-DCP; and (b) 2,6-DCP without and with NaCl over Fe-Cu-PILC (reaction conditions: $[DCP] = 2 \text{ mM}$; $[H_2O_2] = 40 \text{ mM}$; $[catalyst] = 1 \text{ g L}^{-1}$; $[NaCl] = 1 \text{ g L}^{-1}$; and temperature of 40°C).

2,6-DCP oxidation (Figs. 2 and 3). This indicated that the substitution position of chlorine atoms in the aromatic ring determined the decomposition of H_2O_2 and the formation of $\cdot\text{OH}$ and subsequently determined the oxidation and dechlorination of DCPs.

The decomposition process of H_2O_2 is described by following reactions (Kwan and Voelker 2003; Huang and Huang 2008):

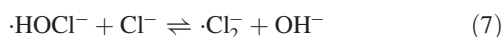




Timofeeva et al. (2005) confirmed by electron spin resonance (ESR) spectra the formation of peroxide-Fe³⁺ complexes upon the interaction of H₂O₂ and Al-Fe-PILC. Also, it was assumed that the reaction in Eq. (4), where pH was lowered by reduction of Fe (III) to Fe (II), was the rate-limiting step (Kwan and Voelker 2003). Obviously, the presence of Fe (II) and a sufficiently acidic catalyst surface are important and necessary for catalyzing the decomposition of H₂O₂ into ·OH [reaction in Eq. (5)], which initiates the oxidation of DCPs. Therefore, the induction period observed during DCP oxidation (Fig. 1 and Table 3) (Catrinescu et al. 2012; Zhou et al. 2014) could be postulated as an activation process involving the complexation of Fe (III) with H₂O₂ and the subsequent reduction decomposition of the complexes.

Ortho-DCPs such as 2,6-DCP have a strong steric hindrance effect that is relatively resistant to free radical attack; besides, O binds to the carbon atom in the first step of oxidation to form a 2,6-dichloro-1,4-benzoquinone and H₂O (Zhou et al. 2011). On the contrary, meta-DCPs such as 3,4-DCP have a strong π-electron-donating conjugative effect that is more susceptible to free radical attack, and 2-chloro-1,4-benzoquinone and HCl form in the first step oxidation (Zhou et al. 2011). The formation of HCl accelerates the activation of the catalytic surface and subsequently shortens the induction period of H₂O₂ decomposition and DCP oxidation. It is noticeable that there are more and faster H₂O₂ decomposition and ·OH formation and subsequent faster DCP oxidation in meta-substitution or parasubstitution than that in orthosubstitution.

The same amount of H₂O₂ decomposition in the presence and absence of NaCl was observed, whether for 3,4-DCP or 2,6-DCP (Fig. 2), but the amount of ·OH production in the former was 10.5% (3,4-DCP) and 21.4% (2,6-DCP) lower than in the latter (Fig. 3), indicating that a certain amount of Cl⁻ could react with ·OH to form some chlorine radicals such as ·Cl₂⁻, as shown in the reactions in Eqs. (6) and (7) (De Laat et al. 2004; De Laat and Le 2006; Pignatello et al. 2006). In particular, during 2,6-DCP oxidation, Cl⁻ appears to play a much more important role in scavenging ·OH due to 21.4% loss in ·OH as compared to control (without NaCl addition)



In fact, Cl⁻ insignificantly affect H₂O₂ decomposition and ·OH formation, and subsequently did not affect the oxidation rate in the 3,4-DCP system, whereas it greatly lengthened the induction period of H₂O₂ decomposition (*T_i* increased from 350 to 510 min) and ·OH formation (*T_i* increased from 300 to 420 min), resulting in significant inhibition of the oxidation process in the 2,6-DCP system (Figs. 1–3 and Table 3). Therefore, we considered that the inhibitory effect of Cl⁻ on ortho-DCP oxidation was mainly due to the inhibition of H₂O₂ decomposition. As stated previously, H₂O₂ is more difficult to complex with Fe (III) and correspondingly decompose into Fe (II) and hydroxyl radicals during 2,6-DCP oxidation than during 3,4-DCP oxidation, and the presence of Cl⁻ in the 2,6-DCP system might aggravate the difficulty due to the competitive complexation of Cl⁻ and H₂O₂ with Fe (III) (De Laat et al. 2004; De Laat and Le 2006; Pignatello et al. 2006).

Fig. 4 shows that in the presence or absence of NaCl, the dechlorination (Cl⁻ release) was the same for both 3,4-DCP and 2,6-DCP oxidation, where about 69% of chlorine atoms were dechlorinated, suggesting that NaCl addition did not affect the dechlorination of

Table 4. Major intermediates during 2, 6-DCP oxidation by H₂O₂ over Fe-Cu-PILC without and with NaCl

Time (min)	Control (without NaCl)	Treatment (with NaCl)
5.588	C ₇ H ₃ O ₃ Cl ₂ , C ₆ H ₃ OCl ₂	C ₇ H ₃ O ₃ Cl ₂ , C ₆ H ₃ OCl ₂
6.304	C ₁₄ H ₁₁ O ₅ Cl ₂	C ₇ H ₃ O ₂ Cl ₂
6.406	C ₁₀ H ₃ O ₄ Cl ₂	C ₁₀ H ₃ O ₄ Cl ₂
6.518	C ₈ H ₅ O ₂ Cl ₂	C ₈ H ₅ O ₂ Cl ₂
6.637	C ₁₄ H ₁₁ O ₅ Cl ₂ , C ₈ H ₁₆ O ₇ Cl ₃	C ₁₄ H ₁₁ O ₅ Cl ₂ , C ₈ H ₁₆ O ₇ Cl ₃
7.139	C ₁₀ H ₇ O ₄ Cl ₂ , C ₆ H ₃ OCl ₂	C ₁₀ H ₇ O ₄ Cl ₂ , C ₆ H ₃ OCl ₂
7.288	C ₁₈ H ₃₃ O ₅	C ₁₈ H ₃₃ O ₅
7.751	C ₁₀ H ₁₂ NO ₃	C ₁₀ H ₁₂ NO ₃

DCPs, and also that a considerable proportion of chlorinated products of DCPs formed during DCP oxidation. Not only chlorination but also hydroxylation took place during CWPO of DCPs, leading to the formation of more complex compounds (Table 4) (Li et al. 1999; Catrinescu et al. 2011; Zhou et al. 2014). Even Catrinescu et al. (2011) thought that high molecular mass compounds (dimers, oligomers) probably formed by oxidative coupling reaction, for example, dichlorodihydroxybiphenyl, dihydroxytrichlorobiphenyl, and so on. However, HPLC-MS analysis showed that there was no difference in major intermediates of 2,6-DCP oxidation without and with NaCl (Fig. 5 and Table 4). The same results were observed for 3,4-DCP oxidation (data not shown). This suggested that addition of NaCl did not change the oxidation path of DCPs, regardless of whether their oxidation rate was inhibited (e.g., 2,6-DCP) or noninhibited (e.g., 3,4-DCP).

The mechanism of catalytic oxidation of organic pollutants by H₂O₂ over Fe-pillared clays is: first, H₂O₂ reaches the clay surface and forms Fe-H₂O₂ surface complexes; second, clay surface protonation (pH decrease) results in the decomposition of H₂O₂ and subsequently the generation of hydroxyl radicals (·OH); third, ·OH attacks the organic pollutants adsorbed on clay surfaces, causing the oxidation of organic pollutants. The influence of chloride ions on catalytic peroxide oxidation of chlorinated phenols is complex. On the one hand, Cl⁻ could accelerate the complexation of H₂O₂ by the salting-out effect of NaCl (Mahamuni and Pandit 2006), especially shortening the induction period by promoting the rate-limiting step of H₂O₂ decomposition (the process of activation via the reduction of active metal species on the catalyst surfaces) (Zhou et al. 2016). On the other hand, Cl⁻ strongly inhibits H₂O₂ decomposition by competing with H₂O₂ for the complexation of active metal species (Pignatello et al. 2006), as well as chlorinated phenol oxidation by scavenging the transitory ·OH (De Laat et al. 2004; De Laat and Le 2006). These two opposite effects of Cl⁻ may depend on the interaction among the catalyst surface, CP, H₂O₂, Cl⁻, active metal species, and ·OH, as shown in Fig. 6.

For ortho-substituted DCPs such as 2,6-DCP with stronger polarity, the stronger competitive adsorption occurred between 2,6-DCP and Cl⁻, leading to less H₂O₂ complexation with Fe(III) and much slower reduction decomposition of Fe(III)H₂O₂. Additionally, Fe(II) probably complexed with Cl⁻ due to the lack of sufficient H₂O₂. Therefore, the generation of ·OH was much less and slower. Further, the hydroxylation of 2,6-DCP did not work well due to strong steric hindrance (Zhang et al. 2003; Zhou et al. 2011), resulting in more ·OH being scavenged by Cl⁻. In other words, the inhibitory effect of Cl⁻ [complexation with ·OH and Fe(II)] became more significant than its promotion effect (salting-out effect and surface activation), so there is significant inhibition of the oxidation rate of 2,6-DCP with NaCl addition. On the contrary, for metasubstituted or parasubstituted DCPs such as 3,4-DCP with stronger nonpolarity, competitive adsorption on the catalyst surface occurred between Cl⁻ and 3,4-DCP, which promoted more

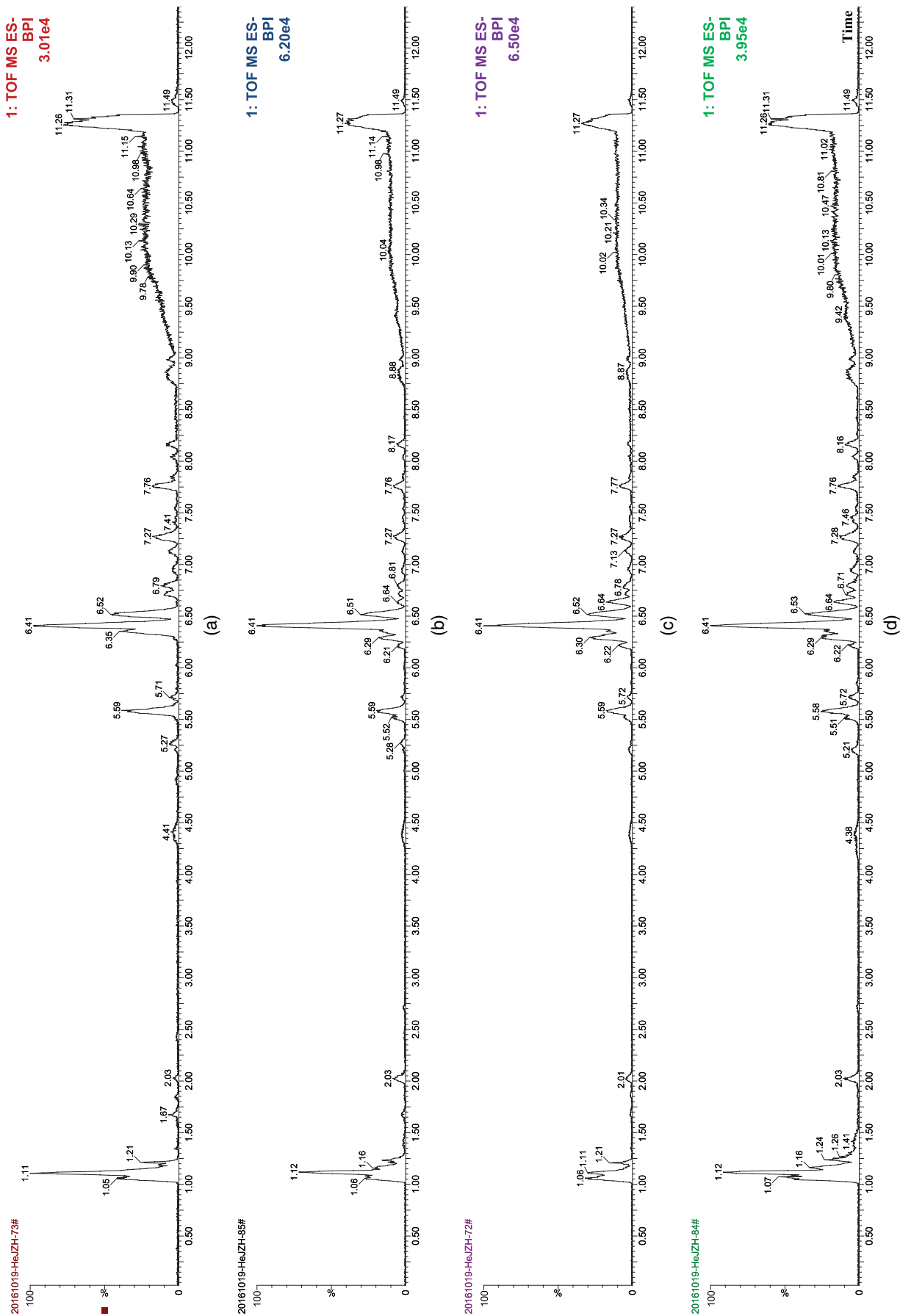


Fig. 5. Chromatograms of HPLC-MS for 2,6-DCP oxidation by H_2O_2 over Fe-Cu-PILC: (a) 90% conversion in absence of NaCl; (b) 90% conversion in presence of NaCl; (c) 50% conversion in absence of NaCl; and (d) 50% conversion in presence of NaCl.

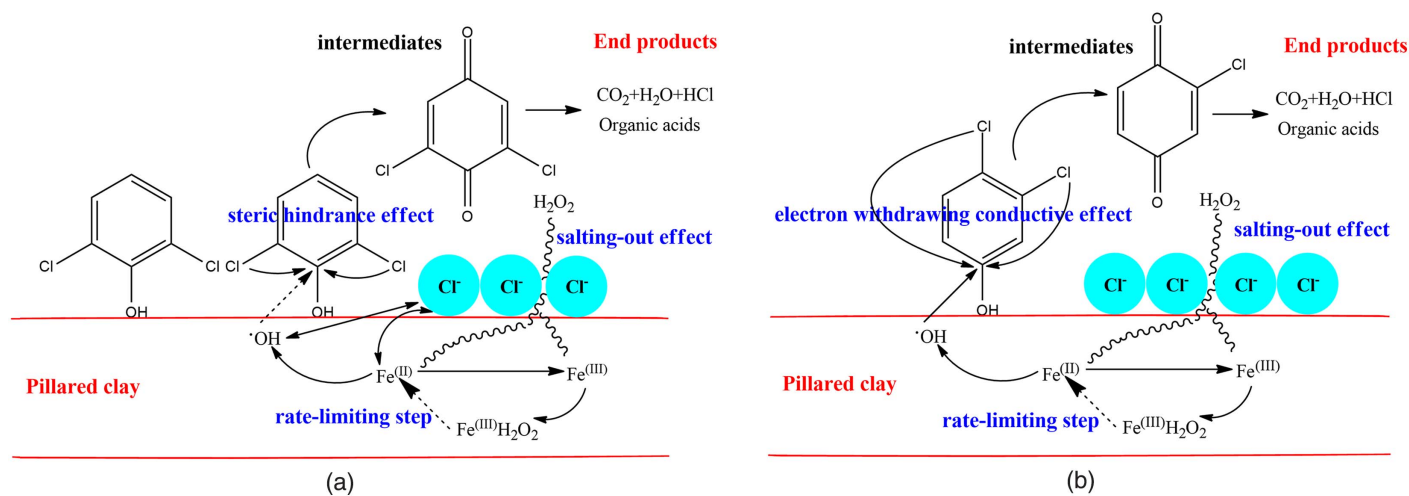


Fig. 6. Proposed mechanism for Cl^- affecting the oxidation rate of DCPs: (a) 2,6-DCP; and (b) 3,4-DCP.

and faster decomposition of H_2O_2 into $\cdot\text{OH}$ and thus faster regeneration of Fe(III) by oxidation reaction between Fe(II) and H_2O_2 . Moreover, it was easier for $\cdot\text{OH}$ to attack 3,4-DCP with the formation of benzoquinone intermediates due to the σ -electron withdrawing conductive effect or π -electron donating conjugative effect of chlorine on the aromatic ring (Zhang et al. 2003; Zhou et al. 2011). Therefore, the inhibitory effect of Cl^- [complexation with $\cdot\text{OH}$ and Fe(II)] was less, but its promotion effect (salting-out effect and surface activation) dominated, suggesting that there is no obvious change in the oxidation rate of 3,4-DCP between without and with NaCl addition. In a previous study (Zhou et al. 2016), it was observed that although Cl^- promoted the oxidation rate of DCPs over CuAl-hydrotalcite and clay composite, the promotion effect on the ortho-position of DCPs such as 2,6-DCP was the least (0.8%), compared to those on metapositions and parapositions such as 3,5-DCP (82.3%) and 2,5-DCP (111.3%). This agrees with the results shown here, implying that this effect of Cl^- on metapositions and parapositions is generally positive (promotion); this effect of Cl^- on ortho-position is generally negative (inhibition).

In general, Cl^- strongly inhibited the oxidation of ortho-substituted chlorophenols but not that of metasubstituted and para-substituted chlorophenols, and the strong inhibitory effect of Cl^- on ortho-DCPs was mainly ascribed to the inhibition of H_2O_2 decomposition by competing with H_2O_2 for active metal sites on the catalyst surface. The actual application of CWPO technology to the degradation of ortho-substituted chlorophenols in saline wastewater should be paid more attention in order to weaken or avoid the undesirable inhibition of H_2O_2 decomposition.

Conclusions

The oxidation of DCPs by H_2O_2 over Fe-Cu-PILC with and without NaCl was studied. The results showed that the presence of Cl^- inhibited the DCP oxidation rate, where T_I was lengthened from 75.9 to 93.6 min, and $T_{1/2}$ was extended to 20.6 min (from 86.6 to 107.2 min), as compared with control (without NaCl addition). However, the inhibitory effect could only occur during oxidation of ortho-substituted chlorophenols such as 2,6-DCP, where T_I was lengthened to 80 min (from 290.7 to 370.4 min), whereas it was almost negligible during oxidation of metasubstituted or parasubstituted chlorophenols. In addition, the presence of Cl^- did not affect the conversion (dechlorination

and hydroxylation) of DCPs. That is, NaCl addition did not change the oxidation path, as evidenced by HPLC-MS. Multiple indicators, including Cl^- release, H_2O_2 decomposition, $\cdot\text{OH}$ formation, and intermediate identification, showed that the inhibitory mechanism of Cl^- on ortho-DCP oxidation was mainly due to inhibiting the rate-limiting step of H_2O_2 decomposition (lengthening the induction period from 350 to 510 min) by competing with H_2O_2 for the complexation of Fe(III), secondary due to scavenging of $\cdot\text{OH}$ to form $\cdot\text{Cl}_2^-$.

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