The activity and selectivity of catalytic peroxide oxidation of chlorophenols over Cu–Al hydrotalcite/clay composite

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ABSTRACT

Liquid phase catalytic oxidation of chlorophenols (CPs) was carried out over Cu–Al hydrotalcite/clay composite at ambient temperature and pressure using hydrogen peroxide as oxidant. The results showed that the catalyst had high catalytic activity, with complete oxidation of 4-CP within 40 min at 40 °C. The content and position of chlorine on the aromatic ring had significantly different effects on the oxidation rate of CPs, with the rate sequence of phenol > monochlorophenol (MCP) > dichlorophenol (DCP) > trichlorophenol (TCP), 3-CP > 2-CP > 4-CP, and 3,5-DCP > 3,4-DCP > 2,5-DCP > 2,4-DCP > 2,6-DCP. This was ascribed to the interactions among σ-electron withdrawing conductive effect, π-electron donating conjugative effect, and steric hindrance effect of chlorine. It was evidenced that the catalytic peroxide oxidation of CPs in the first step was selective and rate-limiting, where chlorinated 1,4-benzoquinones formed.

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1. Introduction

Chlorophenols (CPs) can be found in many ecosystems: surface and ground waters, bottom sediments, atmospheric air, and soils [1]. Most of them have been listed as priority pollutants due to the toxicity and hard biodegradability. Therefore, disposing safely these compounds is becoming an important area of research with the increasing concern about the environment. Various abatement techniques including biological, thermal, and chemical treatments have been developed in the last few years for the detoxification of organic pollutants [2,3]. Among these techniques, catalytic wet peroxide oxidation (CWPO) appears to be a promising field of study, which has been reported to be effective for the near ambient degradation of soluble organic pollutants, because it can provide a nearly complete degradation [4–9].

Active, economical, and stable catalysts would play a critical role in the degradation of organic pollutants in CWPO. In the past 10 years, the attention has been focused on different kinds of supported transition metal ion (iron or copper) catalysts: metal-exchanged zeolites, metal-exchanged clays, metal-exchanged resins, and hydrotalcite-like compounds [8,9]. Compared with iron-based catalysts, copper-based catalysts show higher resistance to leaching and better catalytic performance, and wider range of pH operations [10]. Thus, there has been a considerable interest in the development of copper-based heterogeneous catalysts especially hydrotalcites and pillared clays (PILCs) in recent years. Although they have been widely employed into the peroxide oxidation of phenol, the catalytic oxidation of CPs over these catalysts at ambient temperature and pressure has not been reported. Only a few researchers used iron-based clays or iron-containing minerals especially goethite as catalysts to catalyze the peroxide oxidation of CPs [11–15]. It was found that the catalytic activity was mainly due to leached iron ions from iron-exchanged clays or the reductive dissolution of goethite [11–13], whereas in Fe-PILCs/H_2O_2 systems, CPs reacted with hydroxyl radicals (·OH) produced mainly by the surface-catalyzed decomposition of hydrogen peroxide [14,15].

In addition, Barbeni et al. [16] found that the degradation rates of monochlorophenols (MCPs) decreased in the order 3-chlorophenol (3-CP) > 2-chlorophenol (2-CP) > 4-chlorophenol (4-CP) under the same experimental conditions. Benitez et al. [17] showed that the degradation rate sequence of different CPs was 4-CP > 2,4-dichlorophenol (2,4-DCP) > 2,4,6-trichlorophenol (2,4,6-TCP) > 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) at constant values of initial CP, hydrogen peroxide and ferrous concentration, pH, and temperature. This means that the position and content of Cl substituent on the aromatic ring strongly affected the peroxide oxidation of CPs. That is, the selective oxidation of CPs in early steps would occur when they were attacked by ·OH, which should be regarded as a rate-limiting reaction. However, it is unfortunate that the selective oxidation mechanism of CPs in the early steps is unclear due to the few studies in this area [18,19].

In this work, we, therefore, synthesized a Cu–Al hydrotalcite/clay composite and investigated the reactivity of catalytic peroxide oxidation of CPs under mild conditions. The aim was to clarify the

effect of Cl substituent of the aromatic ring on the CWPO, and evidence the selective oxidation of CPs in the initial step by H_2O_2 over hydrotalcite/clay composite.

2. Materials and methods

2.1. Materials

Na-bentonite and organic compounds including phenol, CPs, and quinones with a minimum purity of 95% were purchased from Alfa Aesar. The other analytical reagents such as $Cu(NO_3)_2 \cdot 3H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, and Na_2CO_3 were purchased from Sinopharm Chemical Reagent Co., Shanghai, China. Deionized water was used in the experiments.

2.2. Preparation and characterization of the catalyst

The hydrotalcite was synthesized by coprecipitation employing metal nitrates as precursors and $NaOH/Na_2CO_3$ as precipitants. The amounts of 250 ml of aqueous Cu^{2+} and Al^{3+} nitrate solutions and 250 ml of $NaOH/Na_2CO_3$ solutions with a $Cu^{2+}/Al^{3+}/OH^-/CO_3^{2-}$ molar ratio of 6/2/16/1 were added dropwise into a dour-neck flask which was stirred vigorously with a magnetic stirrer and was kept at 50 °C using a thermostated water bath. After the addition of solutions was completed, the mixture was continuously stirred and kept at 50 °C for 4 h and then cooled at room temperature.

The hydrotalcite/clay composite was synthesized by a copolymerization method. The hydrotalcite solution was added dropwise into an aqueous suspension of bentonite (2%), which was stirred vigorously with a magnetic stirrer and was kept at 50 °C using a thermostated water bath. The clay was previously dispersed through continuous stirring of the suspension for 24 h, and the ratio of 20 mmol metal (Cu + Al) per gram of clay was required. After the addition of solution was completed, the suspension was left continuously stirring at 50 °C for 4 h, and then aging at room temperature for 24 h. The obtained solid was washed by centrifugation until nitrate free, and then dried at 105 °C for 6 h.

Powder X-ray diffraction (XRD) pattern of the catalyst was recorded using a Shimadzu XRD-7000 diffractometer (Shimadzu Co., Japan) under the following conditions: 40 kV, 30 mA, and $CuK\alpha$ radiation (λ = 0.15405 nm). The sample, as unoriented powder, was continuously scanned at a scan speed of 4° min^{-1} in the range from 3° to 70°. Fourier transform infrared (FTIR) spectrum was obtained in 4000–400 cm^{-1} range with 16 cm^{-1} resolution on a FT/IR 4100 spectrometer (JASCO Benelux BV, The Netherlands) using the KBr pellet technique. In addition, electron microscopy analysis was performed in a Hitachi S-4800 field emission scanning electron

microscope (FE-SEM) (Hitachi Ltd., Japan), equipped with an energy-dispersive X-ray spectroscopy (EDX).

2.3. Experimental process

The catalytic oxidation process of CPs was carried out in a 250-ml three-neck glass flask fitted with a reflux condenser, a magnetic stirrer, and a thermostated water bath. For a typical run, 100 ml CPs (2 mM) and catalyst (0.1 g) in powder form were loaded into the flask. After the reaction mixture was magnetically stirred and heated to the desired temperature (40 °C), hydrogen peroxide (4 mmol) was added at once, which initiated the reaction. During all the oxidation reactions, 5-ml aliquots were withdrawn at selected time intervals, mixed with 0.1 g manganese dioxide for the purpose of eliminating residual H_2O_2 [20,21], and filtered by means of 0.22-μm membranes to analyze the reaction mixture.

The concentration of CPs in the solutions was determined using gas chromatography (GC). GC analysis was performed with an Agilent 7890A GC (Agilent Technologies, USA), equipped with a column of HP-5 (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). The operating parameters were as follows: FID temperature (300 °C), injection port temperature (280 °C), injection mode (splitless), injection volume (1 μl), carrier gas N_2 (>99.999%), constant flow rate (25 ml min^{-1}), and carrier gas pressure at column head (103.4 kPa). Temperature program was 40 °C for 2 min, 10 °C min^{-1} to 180 °C, and then 25 °C min^{-1} to 250 °C.

3. Results and discussion

3.1. Characterization and activity of the catalyst

The powder XRD pattern and FTIR spectrum of the catalyst are shown in Fig. 1a and b, respectively. The XRD pattern exhibited diffraction peaks at 19.8° and 36.1° corresponding to montmorillonite, the diffraction peaks at 21.9° and 28.0° corresponding to quartz [22,23], and the peaks close to 2θ = 11°, 24°, and 35° (actual 10.4°, 24.1°, and 35.6°) characteristic of 3R packing of hydrotalcite layers (Fig. 1a) [24]. FTIR spectrum showed that the strong and broad band at 3436 cm^{-1} was due to the stretching vibration of the H—OH bond of water molecules adsorbed on the solid surface; the absorption at 1635 cm^{-1} was associated with the bending vibration of the H—OH bond of water molecules; the strong band at 1049 cm^{-1} represented the stretching vibration of Si—O—Si groups of the tetrahedral sheet; the band at 470 cm^{-1} corresponded to the bending vibration of Si—O—Si groups [25]; and the active absorption band at 1384 cm^{-1} was assigned to symmetric stretching vibration of the interlayer carbonate anion (Fig. 1b)
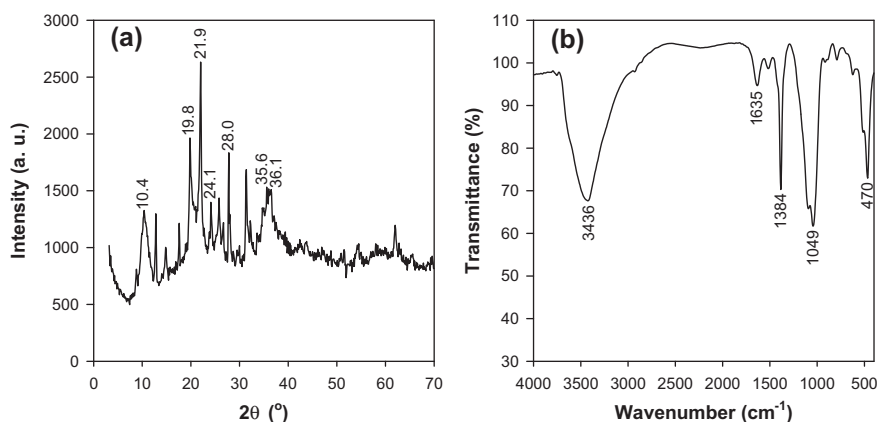

Fig. 1. Powder X-ray diffraction pattern (a) and FTIR spectrum in KBr (b) of hydrotalcite/clay composite.
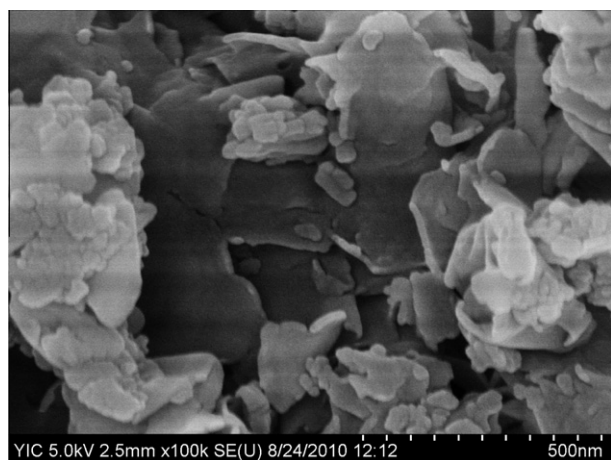
Fig. 2. SEM micrograph of hydrotalcite/clay composite.

[26]. In a word, the XRD pattern and FTIR spectrum indicated that the catalyst was a polymer of hydrotalcite and clay.

The SEM image of the catalyst is shown in Fig. 2. It was found that a composite catalyst was formed via the deposition of hydrotalcite on bentonite surface; moreover, the catalyst surface was not uniform and a large number of cavities and crevices could be clearly observed. Additionally, the chemical composition of catalyst obtained using EDX analysis, given in Table 1, also indicated that the catalyst was a polymer containing Cu–Al hydrotalcite and Na-bentonite.

When it was used in the peroxide oxidation of 4-CP, hydrotalcite/clay composite catalyst exhibited high catalytic activity, as shown in Fig. 3. It was seen that 4-CP could be completely oxidized within 40 min at 40 °C in the coexisting system of catalyst and

Table 1
The chemical composition of catalyst surface measured by EDX.[a]

	C	O	Si	Al	Fe	Cu	Na	Mg	Total
Weight%	15.88	48.73	11.19	4.20	1.14	17.36	1.06	0.44	100.0
Atom%	26.29	55.79	7.82	3.10	0.40	5.43	0.82	0.36	100.0

[a] Standard sample (C, CaCO$_3$; O, SiO$_2$; Si, SiO$_2$; Al, Al$_2$O$_3$; Fe, Fe; Cu, Cu; Na, albite; Mg, MgO).
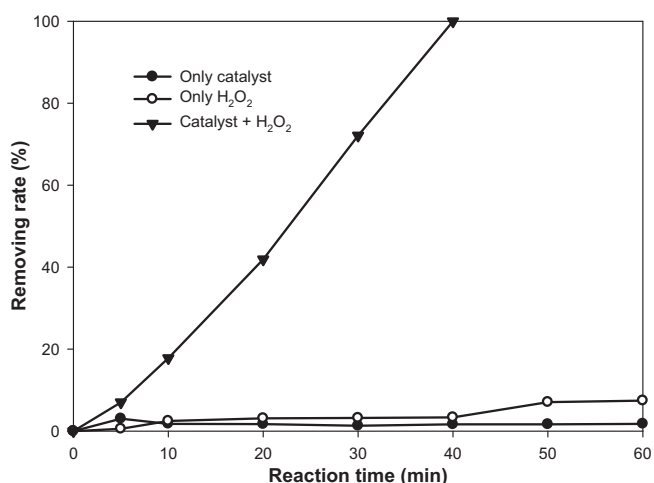

Fig. 3. Kinetics of 4-CP removal by hydrotalcite/clay composite or hydrogen peroxide (4-CP, 2 mM; H$_2$O$_2$, 40 mM; catalyst, 1 g L^{-1}; temperature, 40 °C; pH 6.81).

H$_2$O$_2$. On the contrary, in the presence of single catalyst or H$_2$O$_2$, the removal rate of 4-CP after 60 min was only 1.8% and 7.4%, respectively.

3.2. Influence of H$_2$O$_2$ amount, catalyst dosage, temperature, and pH on the oxidation of 4-CP

Fig. 4 shows the influence of H$_2$O$_2$ amount and catalyst dosage on catalytic oxidation of 4-CP. Although the conversion rate of 4-CP increased with increasing H$_2$O$_2$/4-CP molar ratio from 10 to 25, the increase was not obvious at $n(H_2O_2)/n$ (4-CP) $\geqslant$ 15 (Fig. 4a). On the other hand, when the catalyst dosage was increased from 0.5 to 1.5 g L^{-1}, the conversion rate of 4-CP increased obviously. However, at higher catalyst dosage such as 2.5 g L^{-1} the catalytic oxidation of 4-CP was weakened strongly (Fig. 4b). Thus, during the CWPO reaction there was an appropriate ratio among 4-CP, H$_2$O$_2$, and catalyst, and here, we commended the values as follows: 1.5 g L^{-1} of catalyst and $n(H_2O_2)/n$ (4-CP) = 15 for the oxidation of 2 mM of 4-CP.

The influence of temperature and pH on the conversion of 4-CP is shown in Fig. 5a and b, respectively. At lower temperatures such as 30 °C, there was very low conversion of 4-CP (only 40.4%) within 60 min. The conversion increased rapidly with the increase in temperature, with complete conversion of 4-CP within 40 min at 40 °C and within 20 min at 50 °C, respectively (Fig. 5a). Undoubtedly, higher temperatures (>40 °C) would be unadvisable in view of the cost of the oxidation reaction.

It was found from Fig. 5b that a maximum of catalytic activity was observed at a pH range of 2.77–7.87, where the complete oxidation of 4-CP was achieved within 1 h. The pH range was much wider than that not only in classical Fenton's reactions but also in Fenton-like reactions catalyzed by iron-based heterogeneous catalysts [22,27]. This strongly supported the view of Caudo et al. [10] who considered that copper-based heterogeneous catalysts had a wider range of pH operations. The catalytic oxidation of 4-CP mainly proceeded via an OH-radical mechanism where ·OH was generated by the interaction between active O species on a heterogeneous copper catalyst surface and H$_2$O$_2$ [28]. Probably, to keep their ability to generate ·OH from H$_2$O$_2$, the surface acidity of the heterogeneous catalysts was an important factor. At higher pH (8.81), H$_2$O$_2$ was possibly decomposed to oxygen by the catalyst; at lower pH (1.83) the decomposition of H$_2$O$_2$ was smaller; moreover, the partial catalyst was possibly deactivated due to the increasing leaching of active elements. In a word, a smaller amount of ·OH was generated under the two conditions, resulting in lower conversion rates of 4-CP (60.5% and 72.7%, respectively) (Fig. 5b).

3.3. Selectivity of catalytic peroxide oxidation of CPs

Table 2 summarizes the oxidation rates of different CPs by H$_2$O$_2$ over hydrotalcite/clay composite. It was found that chlorine content of chlorinated phenols had a significant effect on the reactivity of CWPO, with the oxidation rate sequence phenol > MCP > DCP > TCP at constant values of initial compound, hydrogen peroxide, and catalyst concentration. That is, the oxidation reactivity of CPs greatly decreased with increasing substitution of chorine on the aromatic ring. This was consistent with the results obtained by some previous researchers [17,29,30]. Furthermore, the position of chlorine atoms on the aromatic ring has different effects on the oxidation rates of CP isomers with the same chlorine content. For instance, for MCPs, the oxidation of 3-CP is faster than that of 2-CP, which is oxidized more easily than 4-CP; for DCPs, the oxidation rates decreased in the order 3,5-dichlorophenol (3,5-DCP) > 3,4-dichlorophenol (3,4-DCP) > 2,5-dichlorophenol (2,5-DCP) > 2,4-DCP > 2,6-dichlorophenol (2,6-DCP) (Table 2). Barbeni et al. [16] also reported the same degradation rate
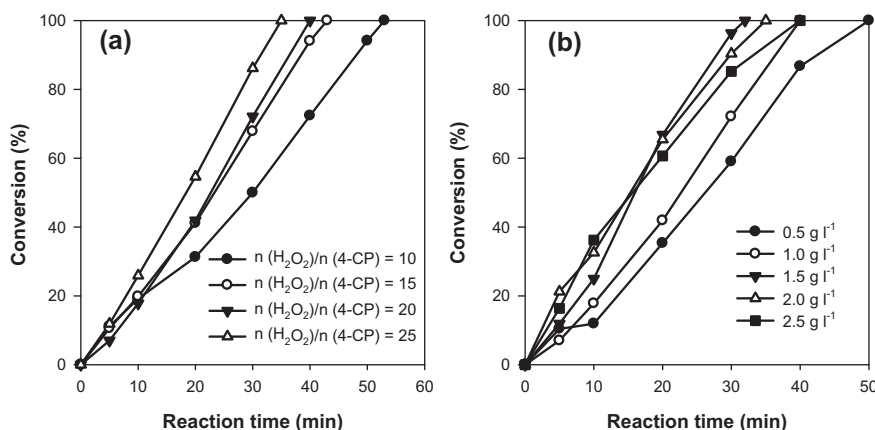
Fig. 4. (a) Influence of H_2O_2 amount on the conversion of 4-CP (4-CP, 2 mM; catalyst, 1 g L^{-1}; temperature, 40 °C; pH 6.81); (b) influence of catalyst dosage on the conversion of 4-CP (4-CP, 2 mM; H_2O_2, 40 mM; temperature, 40 °C; pH 6.81).
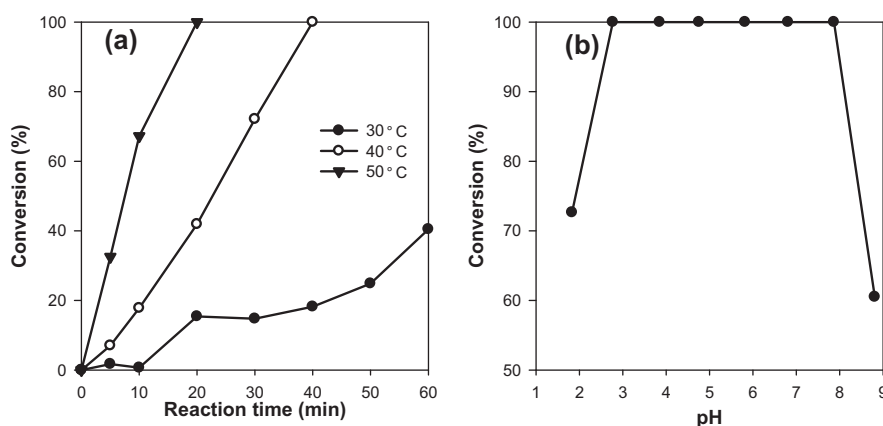

Fig. 5. (a) Influence of temperature on the conversion of 4-CP (4-CP, 2 mM; H_2O_2, 40 mM; catalyst, 1 g L^{-1}; pH 6.81); (b) influence of solution pH on the conversion of 4-CP (4-CP, 2 mM; H_2O_2, 40 mM; catalyst, 1 g L^{-1}; temperature, 40 °C; time 1 h).

Table 2
Time needed for complete oxidation of CPs and their average reaction rates.[a]

Phenolic compound	Time (min)	Average rate (mM min^{-1})
Phenol	13	1.54×10^{-1}
3-CP	17	1.18×10^{-1}
2-CP	32	6.25×10^{-2}
4-CP	40	5.0×10^{-2}
3,5-DCP	60	3.33×10^{-2}
3,4-DCP	65	3.08×10^{-2}
2,5-DCP	120	1.67×10^{-2}
2,4-DCP	150	1.33×10^{-2}
2,6-DCP	300	6.67×10^{-3}
2,4,6-TCP	540	3.70×10^{-3}

[a] Reaction conditions (phenolic compound, 2 mM; H_2O_2, 40 mM; catalyst, 1 g L^{-1}; temperature, 40 °C).

Table 3
Retention times for intermediate products of CPs and standard compounds measured by GC.

Phenolic compound	Retention time (min) for intermediate product	Standard compound and its retention time (min)
Phenol	5.105	1,4-benzoquinone (5.149)
3-CP	7.987	2-chloro-1,4-benzoquinone (8.017)
2-CP	7.993	2-chloro-1,4-benzoquinone (8.017)
4-CP	5.106	1,4-benzoquinone (5.149)
3,5-DCP	10.330	2,6-dichloro-1,4-benzoquinone (10.346)
3,4-DCP	7.988	2-chloro-1,4-benzoquinone (8.017)
2,5-DCP	–	2,5-dichloro-1,4-benzoquinone (10.429)
2,4-DCP	7.995	2-chloro-1,4-benzoquinone (8.017)
2,6-DCP	–	2,6-dichloro-1,4-benzoquinone (10.346)
2,4,6-TCP	10.330	2,6-dichloro-1,4-benzoquinone (10.346)

'–' Means no intermediate product was detected by GC.

sequence of MCPs. However, Tang and Huang [31] reported that the oxidation rate of MCPs decreased according to the order 3-CP > 4-CP > 2-CP. From these examples, we could see that, for different oxidation systems, chlorine substitution on the aromatic ring could cause many different effects on the reactivity of CPs.

The effect of Cl substituent of the aromatic ring on the reactivity of CPs was mainly caused by σ-electron withdrawing conductive effect, π-electron donating conjugative effect, and steric hindrance effect of chlorine [32]. Usually, the impact of π-electron donating conjugative effect of chlorine at *meta* positions was more significant, whereas the impact of steric hindrance effect of chlorine at

ortho positions was more significant. The chorine at *para* position not only produced σ-electron withdrawing conductive effect but also might be dechlorinated when it was attacked by ·OH, which markedly inhibited the oxidation reaction. In conclusion, the more chlorine atoms existing on the aromatic ring especially at *ortho* and *para* position, the more difficult the oxidizing of CP.

(X_1, X_2, X_3 and X_4 represents H and/or Cl, respectively)
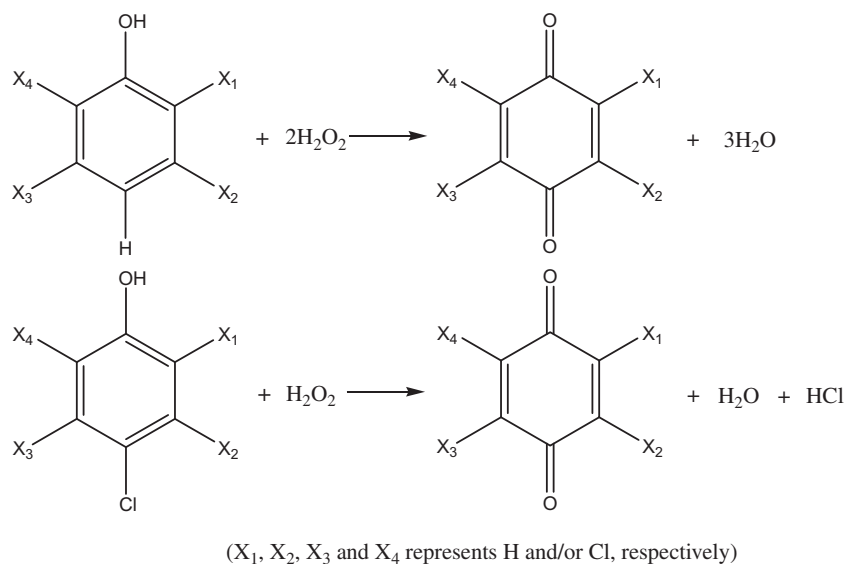
Scheme 1. The reaction equation for the selective oxidation of CPs in the first step.

It is more important that the position of chlorine substituent on the aromatic ring obviously influenced the oxidation selectivity of CPs. Table 3 lists the retention times for intermediate products of CPs and standard compounds. It could be found that the selective oxidation of CPs in the early steps occurred when they were attacked by ·OH, where chlorinated 1,4-benzoquinones formed first. Leyva et al. [18] also showed that at short reaction times, 4-CP was selectively oxidized to 1,4-benzoquinone and 2-CP to 2-chloro-1,4-benzoquinone. Moreover, Lente and Espenson [19] and Shukla et al. [33] evidenced that the first step of the oxidation of 2,4,6-TCP was formation of 2,6-dichloro-1,4-benzoquinone. According to these results, a reaction equation of selective oxidation of CPs in the first step is shown in Scheme 1.

Quinone intermediates, serving as electron shuttles, could play an important catalytic role in the oxidation of aromatic compounds [34,35], or promote the decomposition of H_2O_2, resulting in the formation of ·OH [36,37]. In a word, after chlorinated quinones formed, the oxidation of CPs would be easier. Thus, the content of chlorinated 1,4-benzoquinones was very low, and even was not detected. Herein, it could be concluded that the selective oxidation of CPs in the first step, namely, the formation of chlorinated 1,4-benzoquinones, was a rate-limiting reaction, which strongly determined the whole oxidation rate. Cl substituent at the *ortho* position of CPs might strongly inhibit the oxidation of C—OH to C=O by steric hindrance effect; Cl substituent at the *para* position might inhibit significantly the oxidation of C—Cl to C=O by not only σ-electron withdrawing conductive effect but also the dechlorination. Comparing the two conditions, the selective oxidation rate of CPs with chlorine at *meta* position was the rapidest, because π-electron donating conjugative effect might counteract the negative impact of σ-electron withdrawing conductive effect to some extent, and because steric hindrance effect was smaller.

4. Conclusions

A Cu–Al hydrotalcite/clay composite was prepared and characterized by XRD, FTIR, and SEM, and was applied to the peroxide oxidation of CPs under mild conditions. The results revealed that the catalyst had high catalytic activity, with complete oxidation of 4-CP within 40 min at 40 °C. A feasible reaction system could be proposed as follows: 1.5 g L^{-1} of catalyst, $n(H_2O_2)/n$ (4-CP) = 15, temperature of 40 °C, 2 mM of 4-CP, pH range of 2.77–7.87, and time of 1 h. Furthermore, the content and position of chlorine on the aromatic ring had significantly different effects on the oxidation rate of CPs due to the σ-electron withdrawing conductive effect, π-electron donating conjugative effect, and steric hindrance effect of chlorine, with the rate sequence of phenol > MCP > DCP > TCP, 3-CP > 2-CP > 4-CP, and 3,5-DCP > 3,4-DCP > 2,5-DCP > 2,4-DCP > 2,6-DCP. The catalytic peroxide oxidation reaction of CPs in the first step was selective and rate-limiting, where chlorinated 1,4-benzoquinones formed.

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