

## Chloride ions promoted the catalytic wet peroxide oxidation of phenol over clay-based catalysts

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### ABSTRACT

Catalytic wet peroxide oxidation (CWPO) of phenol over clay-based catalysts in the presence and absence of NaCl was investigated. Changes in the  $\text{H}_2\text{O}_2$ ,  $\text{Cl}^-$ , and dissolved metal ion concentration as well as solution pH during phenol oxidation were also studied. Additionally, the intermediates formed during phenol oxidation were detected by liquid chromatography-mass spectroscopy and the chemical bonding information of the catalyst surfaces was analyzed by X-ray photoelectron spectroscopy (XPS). The results showed that the presence of  $\text{Cl}^-$  increased the oxidation rate of phenol up to 155%, and this phenomenon was ubiquitous during the oxidation of phenolic compounds by  $\text{H}_2\text{O}_2$  over clay-based catalysts.  $\text{Cl}^-$ -assisted oxidation of phenol was evidenced by several analytical techniques such as MS and XPS, and it was hypothesized that the rate-limiting step was accelerated in the presence of  $\text{Cl}^-$ . Based on the results of this study, the CWPO technology appears to be promising for applications in actual saline phenolic wastewater treatment.

**Key words** | catalytic wet peroxide oxidation (CWPO), chloride-assistance, induction period, rate-limiting step, surface modification

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### INTRODUCTION

Over the last few years, catalytic wet peroxide oxidation (CWPO) has been regarded as one of the most promising technologies for the abatement of toxic organic compounds in wastewater. In this method, hydroxyl radicals ( $\bullet\text{OH}$ ) generated via the catalytic decomposition of  $\text{H}_2\text{O}_2$  promote the degradation of organics in wastewater (Liotta *et al.* 2009; Garrido-Ramírez *et al.* 2010; Rokhina & Virkutyte 2011). Fe- and Cu-pillared clays (PILCs), in particular, have been widely used as heterogeneous catalysts for the CWPO reactions of phenolic substrates, in view of their outstanding advantages such as low cost, widespread availability, good rate of conversion, wide operating range of pH, and no or marginal leaching of active ions (Kurian & Sugunan 2006; Liotta *et al.* 2009; Rokhina & Virkutyte 2011; Galeano *et al.* 2014). A variety of highly-efficient PILCs have been prepared and the influences of various operating parameters as well as the role of reactive oxidizing species in determining the activity of the catalysts have been investigated. In addition, the phenol degradation path and the mechanisms of catalytic oxidation have been elucidated, and the potential for the use of CWPO in future has been evaluated

(Kurian & Sugunan 2006; Liotta *et al.* 2009; Rokhina & Virkutyte 2011; Galeano *et al.* 2014). Despite the vast amount of work conducted so far, there are still significant knowledge gaps in the understanding of the kinetic processes and interaction mechanisms of the complicated Fenton-like oxidation reaction.

In previous study (Zhou *et al.* 2013a), we found that the presence of inorganic chlorides significantly increased the oxidation rate of phenol over Cu-Ni-Al hydrotalcite. Micó *et al.* (2013) and Mahamuni & Pandit (2006) also observed similar phenomena during the photo-Fenton oxidation of pesticides and ultrasonic degradation of phenol at high concentration of NaCl solutions, respectively. It is novel and deserves to be paid attention to, because it is usually thought that the presence of inorganic salts such as chlorides, sulphates and nitrates during the CWPO reaction inhibits the oxidation process by scavenging the transitory of  $\bullet\text{OH}$  (De Laat *et al.* 2004; De Laat & Le 2006). Vione *et al.* (2005) observed that phenol chlorination might occur in the presence of dissolved Fe (III),  $\text{H}_2\text{O}_2$ , and  $\text{Cl}^-$ , which in turn may enhance the oxidation of phenolic compounds via the

formation of chlorinated intermediates that act as electron shuttles (Chen & Pignatello 1997; Du *et al.* 2006). Further, Micó *et al.* (2013) attributed the enhancement of  $\text{Cl}^-$  to the participation of  $\bullet\text{Cl}$  in the reaction, whose reaction capacity is comparable to that of  $\bullet\text{OH}$ . However, Mahamuni & Pandit (2006) concluded that NaCl was responsible for only physically pushing the phenol towards the cavity/water interface, owing to the salting-out effect and was not taking part in any chemical reactions. It is obvious that  $\text{Cl}^-$  exerts a complex effect on the CWPO reaction of phenol, and its mechanism is still unclear.

Herein, the role of  $\text{Cl}^-$  in the mediator-assisted CWPO reaction of phenol over clay-based catalysts has been investigated. The aim of this study was two-fold: (1) to present evidence confirming that the promotion of phenol oxidation by  $\text{Cl}^-$  is a ubiquitous phenomenon which still occurs even in high salt (0.17 M NaCl solution); and (2) to reveal the mechanism involved in  $\text{Cl}^-$ -assisted phenol oxidation, which would help extend the applications of the CWPO technology to the treatment of actual saline phenol-containing wastewater.

## EXPERIMENTAL

### Clay-based catalysts

Using common copolymerization procedures, a series of clay materials ( $\text{Cu}_{4.8}\text{Ni}_{1.2}\text{Al}_2$ -hydrotalcite,  $\text{Cu}_6\text{Al}_2$ -hydrotalcite/clay composite and  $\text{Al}_5\text{-Fe}_{0.5}\text{-Cu}_{0.5}$ -pillared clay) were synthesized and characterized in our previous studies (Zhou *et al.* 2011a, 2011b; 2014). These materials, which exhibit both high catalytic activity and high stability, are capable of promoting complete oxidation of phenol or 4-chlorophenol (4-CP) within 2 h at 30–40 °C. Therefore, these materials were used in this work, as high-efficiency heterogeneous catalysts.

### Catalytic oxidation of phenol by $\text{H}_2\text{O}_2$

Following the method described in the previous studies (Zhou *et al.* 2011a, 2011b; 2014), the catalytic oxidation reaction was carried out in a 500-mL three-neck glass flask fitted with a reflux condenser, magnetic stirrer and thermostated water bath. For a typical run, 250 mL of phenol (2.66 mM) and 0.25 g of catalyst in the powder-form were loaded into the flask. The reaction mixture was magnetically stirred and heated to 30 °C, following which  $\text{H}_2\text{O}_2$  (10 mmol) was added immediately, to initiate the catalytic

oxidation reaction. During the oxidation reaction, 10 mL aliquots were withdrawn at certain time intervals, and divided into two 5 mL portions. One of these portions was mixed with 0.1 g  $\text{MnO}_2$  in order to eliminate residual  $\text{H}_2\text{O}_2$  (Liu & Chen 2009), then filtered and analyzed the concentrations of phenol, total organic carbon (TOC),  $\text{Cl}^-$  and dissolved metals (Fe and Cu); whereas the other portion was directly filtered to determine the residual amount of  $\text{H}_2\text{O}_2$ . After reaction, the catalyst was separated from the reaction mixture by centrifugation and air-dried prior to X-ray photoelectron spectroscopy (XPS) analysis.

### Analytical methods

Prior to gas chromatography (GC) analysis, phenol in aqueous solution was extracted by  $\text{CH}_2\text{Cl}_2$ , and then its concentration was determined using an Agilent 7890A GC, following the previous method (Zhou *et al.* 2011a). Other analysis in aqueous solution was done, where TOC content was measured using a Shimadzu TOC-5000 Analyzer; dissolved metals were determined by inductively coupled plasma-mass spectroscopy (ICP-MS; ELAN DRC II); the  $\text{Cl}^-$  was measured by ion chromatography (Dionex ICS3000);  $\text{H}_2\text{O}_2$  content was analyzed by a spectrophotometric method using ammonium metavanadate (Nogueira *et al.* 2005). Additionally, solution pH was monitored every two seconds during reaction process with a Metrohm 888 Titrando. The phenol conversion process and the appearance of intermediates were detected by ion-trap liquid chromatography-mass spectroscopy (LC-MS; LCQ Fleet). Atomic concentration and chemical bonding information were obtained from the catalyst surfaces before and after the CWPO reaction by XPS (Thermo K-Alpha XPS).

## RESULTS AND DISCUSSION

### Oxidation of phenol promoted by $\text{Cl}^-$

In previous study (Zhou *et al.* 2011a), we found that the presence of  $\text{NaNO}_3$  markedly decreased the oxidation rate of phenol over Cu-Ni-Al hydrotalcite, whereas the presence of  $\text{Cl}^-$  significantly increased the oxidation rate. Table 1, which shows that the rates of oxidation of phenol over three types of clay-based catalysts increased markedly in the presence of  $\text{Cl}^-$ , further supports the results from the previous study. The maximum increase in the rate of oxidation of phenol was 155% in the presence of 10 g  $\text{L}^{-1}$  (0.17 M) of NaCl, whereas the oxidation rate decreased

**Table 1** | Influence of inorganic salts on phenol oxidation by H<sub>2</sub>O<sub>2</sub> over different heterogeneous catalysts (Reaction conditions: [phenol] = 2.66 mM; n (H<sub>2</sub>O<sub>2</sub>)/n (phenol) = 15; [catalyst] = 1 g L<sup>-1</sup>; temperature of 30 °C)

Catalyst <sup>a</sup>	Salt		Time (min)	Conversion (%)	Average rate (mM min <sup>-1</sup> )	Increase rate (%)
	Type	Concentration (mM)				
A	Control	0	90	100	2.95 × 10 <sup>-2</sup>	–
	NaCl	17.11	60	100	4.42 × 10 <sup>-2</sup>	49.8
	NaCl	102.66	40	100	6.64 × 10 <sup>-2</sup>	125.1
	KCl	13.41	60	94.4	4.18 × 10 <sup>-2</sup>	41.7
	NH <sub>4</sub> Cl	18.69	90	100	2.95 × 10 <sup>-2</sup>	0
	CaCl <sub>2</sub>	9.01	60	100	4.42 × 10 <sup>-2</sup>	49.8
	MgCl <sub>2</sub>	10.50	60	98.9	4.38 × 10 <sup>-2</sup>	48.5
	NaBr	9.72	120	19.8	4.39 × 10 <sup>-3</sup>	–85.1
	NaNO <sub>3</sub>	11.77	120	41.3	9.14 × 10 <sup>-3</sup>	–69.0
B	Control	0	90	99.2	2.93 × 10 <sup>-2</sup>	–
	NaCl	8.56	60	91.4	4.05 × 10 <sup>-2</sup>	38.2
	NaCl	17.11	60	97.8	4.33 × 10 <sup>-2</sup>	47.8
	KCl	13.41	60	93.8	4.16 × 10 <sup>-2</sup>	41.9
	NH <sub>4</sub> Cl	18.69	90	99.0	2.93 × 10 <sup>-2</sup>	0
	NH <sub>4</sub> Cl	28.04	60	95.0	4.21 × 10 <sup>-2</sup>	43.7
	CaCl <sub>2</sub>	9.01	60	100	4.42 × 10 <sup>-2</sup>	50.9
	MgCl <sub>2</sub>	10.50	60	75.8	3.36 × 10 <sup>-2</sup>	14.6
	NaBr	9.72	120	18.8	4.16 × 10 <sup>-3</sup>	–85.8
C	Control	0	55	27.0	1.31 × 10 <sup>-2</sup>	–
	NaCl	17.11	55	34.7	1.68 × 10 <sup>-2</sup>	28.2
	NaCl	171.11	55	69.1	3.34 × 10 <sup>-2</sup>	155.0
	NaBr	9.72	120	18.1	4.01 × 10 <sup>-3</sup>	–69.3

<sup>a</sup>A: Cu<sub>4.8</sub>Ni<sub>1.2</sub>Al<sub>2</sub>-hydrotalcite; B: Cu<sub>6</sub>Al<sub>2</sub>-hydrotalcite/clay composite; C: Al<sub>5</sub>-Fe<sub>0.5</sub>-Cu<sub>0.5</sub>-pillared clay (500).

greatly in the presence of NaBr and NaNO<sub>3</sub>. These results have significant implications for the possible application of the CWPO technology in phenolic wastewater treatment, considering the high Cl<sup>-</sup> concentration in phenolic wastewater. In other words, the results suggest that the CWPO technology can be extended to actual saline phenol-containing wastewater treatment. In addition, mono-, di-, and trichlorophenols (MCPs, DCPs and TCPs) were also found to undergo Cl<sup>-</sup>-assisted oxidation over the clay-based catalyst considered in this study (Table 2). Cl<sup>-</sup>-assisted oxidation appears to be a novel and ubiquitous phenomenon, in particular Cl<sup>-</sup>-assisted oxidation of CPs has never been observed previously, because it is widely accepted that Cl<sup>-</sup> inhibits Fenton-like processes by scavenging •OH or by competing with H<sub>2</sub>O<sub>2</sub> for the complexation of Fe(III) (De Laat & Le 2006; Pignatello *et al.* 2006), and even the inhibitory effect is noticeable only at Cl<sup>-</sup> concentrations higher than 0.01 M (Pignatello *et al.* 2006; Machulek *et al.* 2007). However, this study shows that even in the presence of 10 g L<sup>-1</sup> of NaCl (0.17 M Cl<sup>-</sup>), which is a much higher concentration, phenol oxidation is in fact promoted, and moreover, the rates of phenol oxidation increased obviously with increasing Cl<sup>-</sup> concentration (Table 1). Therefore, Cl<sup>-</sup>

plays an important role in promotion of the oxidation reactions of phenolic compounds, and this novel finding deserves attention.

Moreover, in the present study, the presence of Cl<sup>-</sup> accelerated the conversion of phenol and its main intermediate, *p*-benzoquinone, into low-molecular weight organic acids. The rate of conversion of phenol increased with increase in the concentration of NaCl (Figure 1). Further, it is observed from Figure 1 that concentration of Cl<sup>-</sup> also alters the composition of the dominant organic acids formed. For example, acetic acid (RT = 2.99 min) and acrylic acid (RT = 1.05 min) were the predominant products after reaction for 120 min in the absence of NaCl, whereas in the presence of 10 g L<sup>-1</sup> of NaCl, oxalic acid (RT = 1.47 min), rather than acrylic acid, became the second most dominant organic acid. This implies that faster and more complete oxidation of phenol occurred in the presence of NaCl, since oxalic acid is more stable compared to acrylic acid. However, no difference was observed in the final TOC conversion (%) in the presence and absence of NaCl (Supplementary, Figure S1), suggesting that Cl<sup>-</sup> only played a major role in increasing the oxidation rate of phenol (conversion), and

**Table 2** | The oxidation of chlorophenols (CPs) by H<sub>2</sub>O<sub>2</sub> over Cu<sub>6</sub>Al<sub>2</sub>-hydrotalcite/clay composite in the absence and presence of NaCl (Reaction conditions: [CP] = 2 mM; n (H<sub>2</sub>O<sub>2</sub>)/n (CP) = 20; [catalyst] = 1.0 g L<sup>-1</sup>; [NaCl] = 1 g L<sup>-1</sup>; temperature of 40 °C)

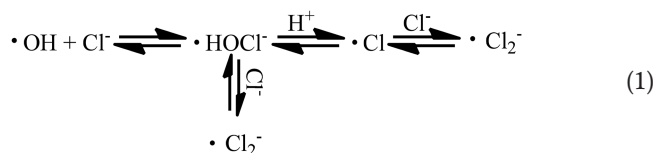
Chlorophenol (CP)	NaCl	Time (min)	Average rate (mM min <sup>-1</sup> )	Increase rate (%)
3-CP	Without	10	1.02 × 10 <sup>-1</sup>	–
3-CP	With	10	1.64 × 10 <sup>-1</sup>	60.8
2-CP	Without	20	6.53 × 10 <sup>-2</sup>	–
2-CP	With	20	8.83 × 10 <sup>-2</sup>	35.2
4-CP	Without	30	5.07 × 10 <sup>-2</sup>	–
4-CP	With	30	5.91 × 10 <sup>-2</sup>	16.6
3,4-DCP	Without	30	4.39 × 10 <sup>-2</sup>	–
3,4-DCP	With	30	6.23 × 10 <sup>-2</sup>	41.9
3,5-DCP	Without	20	4.86 × 10 <sup>-2</sup>	–
3,5-DCP	With	20	8.86 × 10 <sup>-2</sup>	82.3
2,5-DCP	Without	30	2.56 × 10 <sup>-2</sup>	–
2,5-DCP	With	30	5.41 × 10 <sup>-2</sup>	111.3
2,4-DCP	Without	90	1.74 × 10 <sup>-2</sup>	–
2,4-DCP	With	90	2.07 × 10 <sup>-2</sup>	19.0
2,6-DCP	Without	180	8.98 × 10 <sup>-3</sup>	–
2,6-DCP	With	180	9.05 × 10 <sup>-3</sup>	0.8
2,4,6-TCP	Without	300	5.58 × 10 <sup>-3</sup>	–
2,4,6-TCP	With	300	5.95 × 10 <sup>-3</sup>	6.6

did not significantly influence its deep oxidation (mineralization).

The above discussion on the role of Cl<sup>-</sup> suggests that the presence of Cl<sup>-</sup> could be expected to increase the oxidation rate of toxic organic compounds such as phenol, chlorophenols, bisphenol A and pesticides in CWPO or other advanced oxidation processes, in particular photo-degradation due to the formation of high active chlorine and radicals besides of •OH (Vione *et al.* 2005; Micó *et al.*

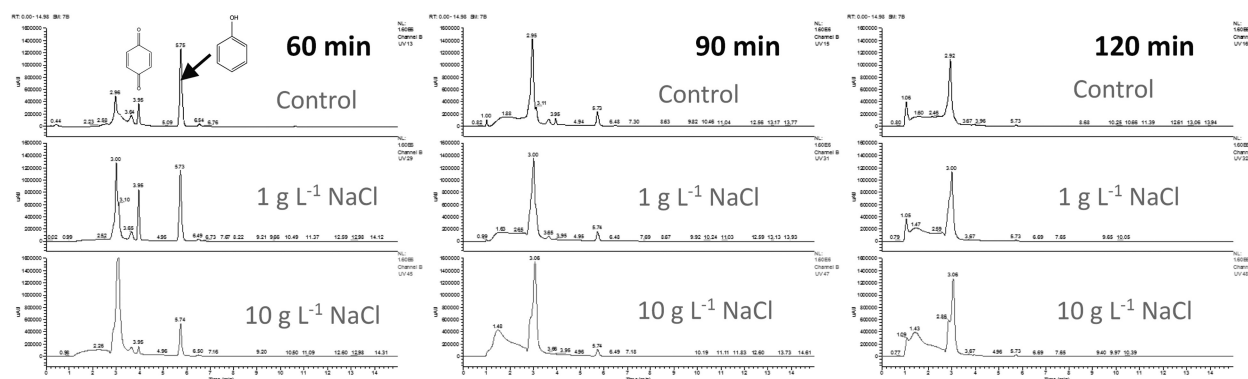
2013; Xiao *et al.* 2015; Zhou *et al.* 2015). In other words, the heterogeneous catalytic oxidation technologies were expected to extend to actual saline wastewater. However, Table 1 showed that NH<sub>4</sub>Cl results are not closer with respect to the rest, the reason for which is not clear. What is more important is that NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> are also presence in actual saline wastewater, which would undoubtedly weaken the effect somewhat of Cl<sup>-</sup>. Maybe this technology should be firstly tried to apply to organic wastewater with NaCl as dominant salt components.

In fact, Micó *et al.* (2013) also observed a similar phenomenon during the photo-Fenton oxidation of pesticides at high salinities. However, they attributed the enhancement in pesticide depletion to the participation of •Cl in the reaction, since the rate constants for the reactions of organic compounds with •Cl were comparable to those with •OH. However, it was almost impossible to generate •Cl in reaction systems near neutral pH in view of reaction (1) (Pignatello *et al.* 2006), which involves not only the consumption of •OH, but also the formation of less reactive •Cl<sub>2</sub><sup>-</sup>.

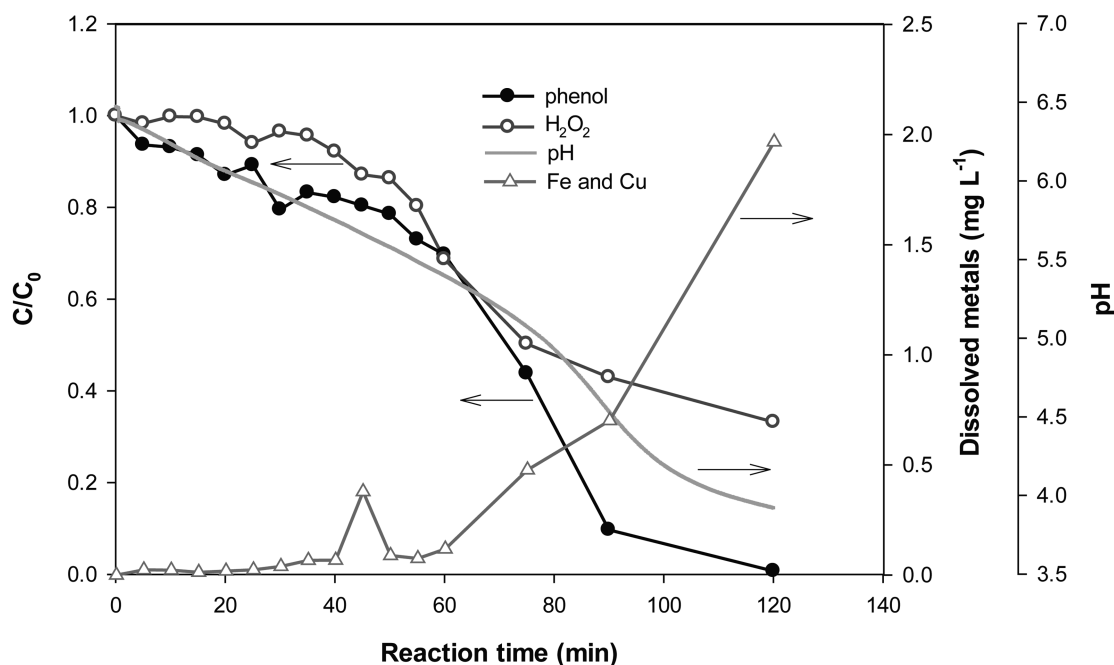


### Mechanism of the enhancement of phenol oxidation rate by Cl<sup>-</sup>

Figure 2 illustrates the interdependence among H<sub>2</sub>O<sub>2</sub> decomposition, phenol oxidation, metallic dissolution, and pH change. Obviously, active metal dissolution was not the reason for the initiation of the oxidation of phenol, as suggested by Belaroui & Bengueddach (2012). The results shown in Figure 2 suggest that the decrease in pH caused



**Q1 Figure 1** | Chromatograms of LC-MS for phenol oxidation by H<sub>2</sub>O<sub>2</sub> over Al<sub>5</sub>-Fe<sub>0.5</sub>-Cu<sub>0.5</sub>-PILC (500) under different NaCl addition after 60 min (left), 90 min (middle) and 120 min (right) (Reaction conditions: [phenol] = 2.66 mM; [H<sub>2</sub>O<sub>2</sub>] = 40 mM; [catalyst] = 1 g L<sup>-1</sup>; temperature of 30 °C).



**Figure 2** | Kinetic profiles of H<sub>2</sub>O<sub>2</sub> decomposition, metallic dissolution and pH changes during catalytic reaction of phenol over Al<sub>5</sub>-Fe<sub>0.5</sub>-Cu<sub>0.5</sub>-PILC (500) (Reaction conditions: [phenol] = 2.66 mM; [H<sub>2</sub>O<sub>2</sub>] = 40 mM; [catalyst] = 1 g L<sup>-1</sup>; temperature of 30 °C).

by the surface-catalyzed reaction is responsible for initiating the oxidation of phenol, because phenol was almost oxidized completely (90.3%), whereas metal dissolution rate was very low (only 0.7 mg L<sup>-1</sup>) in 90 min. Thus, the induction period that is often observed should be attributed to the activation of the catalyst surface, as described in the following reactions (2-4) (Kwan & Voelker 2003; Huang & Huang 2008):

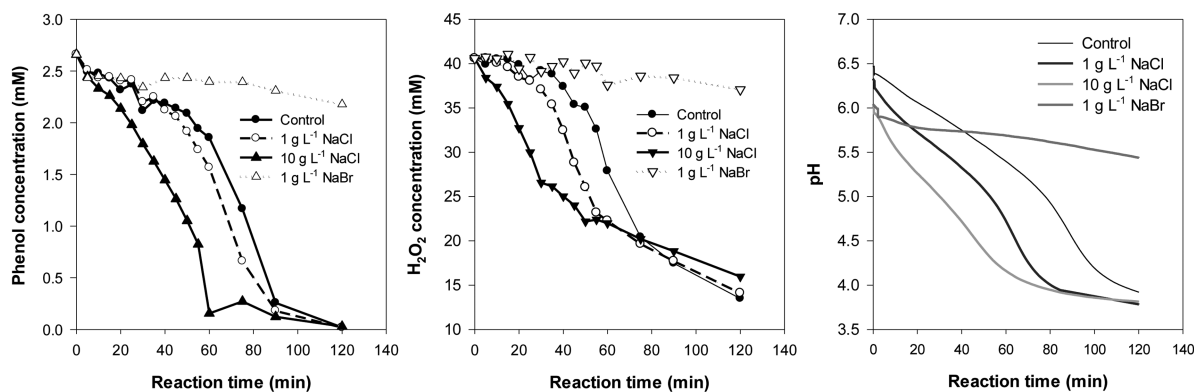


Timofeeva *et al.* (2005) confirmed the formation of peroxide-Fe<sup>3+</sup> complexes upon the interaction of H<sub>2</sub>O<sub>2</sub> and Al-Fe-PILC, by ESR and DR-UV-Vis spectra. It was also assumed that reaction (3), where the pH is lowered as a result of the reduction of Fe (III) to Fe (II), is the rate-limiting step (Kwan & Voelker 2003). Therefore, the presence of Fe (II) and a sufficiently acidic catalyst surface are important and necessary for catalyzing the decomposition of H<sub>2</sub>O<sub>2</sub> into •OH (reaction 4), and for initiating the oxidation of phenol. Tatibouët *et al.* (2005) also found that the pH of the reaction played an important role in the generation of

•OH, which reached a maximum at pH values around 3.7. In view of the above results, the induction period could be postulated as an activation process involving the complexation of Fe (III) with H<sub>2</sub>O<sub>2</sub> and the subsequent reduction-decomposition of the complexes. In addition, lower the pH, shorter would be the induction time. In short, at the initial stage of the catalytic reaction (induction period), the pH decreased monotonously during the adsorption and subsequent decomposition of H<sub>2</sub>O<sub>2</sub>, with little •OH formation and therefore, only slight oxidation of phenol. On the other hand, after the induction period, a large number of •OH radicals were generated, resulting in the fast and complete oxidation of phenol.

Phenol oxidation, H<sub>2</sub>O<sub>2</sub> decomposition, and pH decrease were observed to exhibit a highly consistent relationship in the presence and absence of NaCl (Figure 3). In other words, compared with the control sample (without NaCl), faster decomposition of H<sub>2</sub>O<sub>2</sub> and thus, faster decrease in pH were observed in the presence of NaCl, resulting in the faster oxidation of phenol. Thus, it was considered that the presence of Cl<sup>-</sup> promoted the rate of oxidation of phenol by accelerating the rate-limiting step of the surface-catalyzed decomposition of H<sub>2</sub>O<sub>2</sub> (reaction 3).

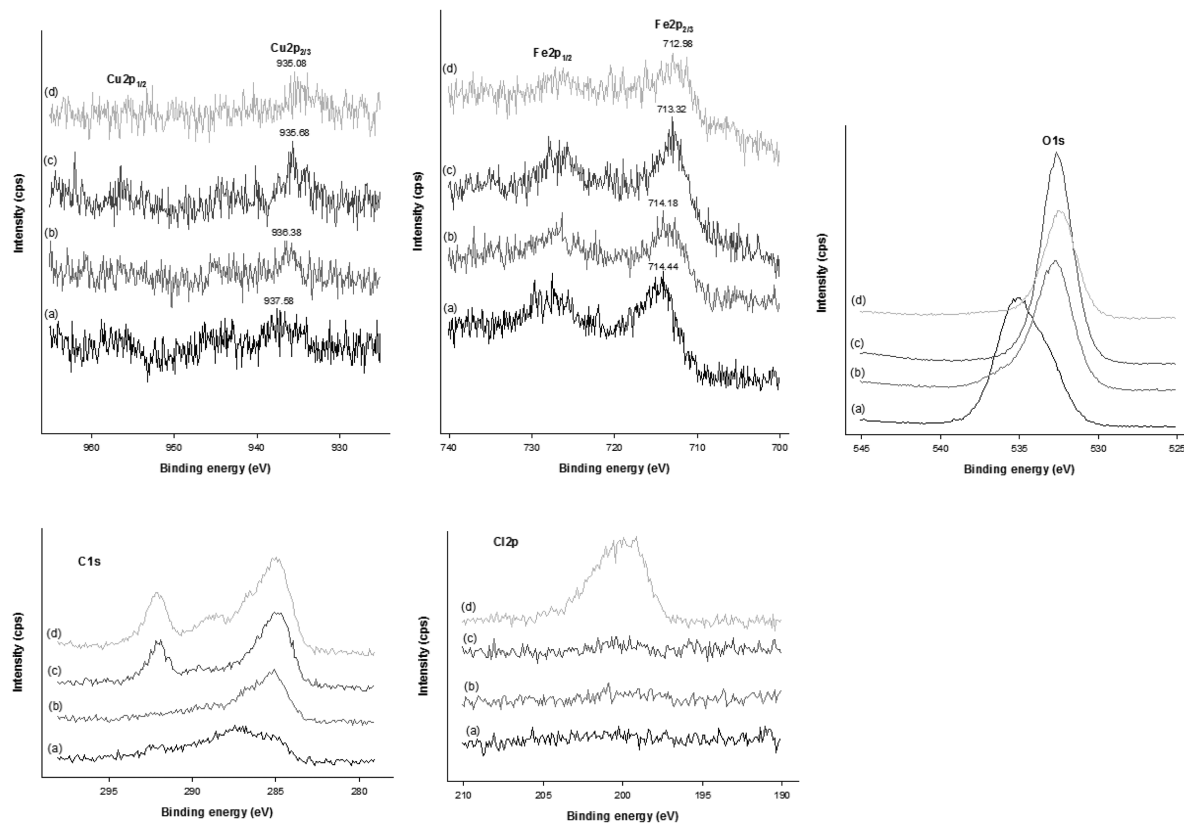
Further, the O/Fe atomic ratio decreased markedly by 13.5 in the presence of 10 g L<sup>-1</sup> of NaCl compared with the control (Table 3), indicating a more reductive environment for the degradation of phenol. Additionally, in the



**Figure 3** | Profiles of phenol oxidation, H<sub>2</sub>O<sub>2</sub> decomposition and pH change during catalytic reaction of phenol over Al<sub>5</sub>-Fe<sub>0.5</sub>-Cu<sub>0.5</sub>-PILC (500) under different NaCl addition (Reaction conditions: [phenol] = 2.66 mM; [H<sub>2</sub>O<sub>2</sub>] = 40 mM; [catalyst] = 1 g L<sup>-1</sup>; temperature of 30 °C).

**Table 3** | The content (atom %) of main elements and atomic ratios (O/Fe, C/Fe and Cl/Fe) of Al<sub>5</sub>-Fe<sub>0.5</sub>-Cu<sub>0.5</sub>-PILC (500) measured by XPS before and after catalytic oxidation of phenol by H<sub>2</sub>O<sub>2</sub> with and without NaCl

System	O1s	Si2p	Al2p	C1s	Fe2p	Cl2p	Na1s	O/Fe	C/Fe	Cl/Fe
Control (before)	53.41	18.14	12.36	9.99	1.37	1.18	–	38.88	7.27	0.86
Control (after)	52.90	16.95	13.27	13.02	1.40	0.88	–	37.80	9.30	0.63
1 g L <sup>-1</sup> NaCl	49.86	17.24	11.54	12.82	1.48	1.42	–	33.67	8.66	0.96
10 g L <sup>-1</sup> NaCl	35.79	10.60	6.95	25.90	1.47	4.19	4.34	24.32	17.60	2.85



**Q2 Figure 4** | XPS spectra of Cu2p, Fe2p, O1s, C1s and Cl2p spectral regions of Al<sub>5</sub>-Fe<sub>0.5</sub>-Cu<sub>0.5</sub>-PILC (500) before and after catalytic oxidation of phenol by H<sub>2</sub>O<sub>2</sub> with and without NaCl (Control before reaction; (b) Control after reaction; (c) 1 g L<sup>-1</sup> NaCl; (d) 10 g L<sup>-1</sup> NaCl).

XPS spectra of the catalyst surface, apparent chemical shifts to lower binding energies were also observed in Figure 4 in the presence of NaCl. Chemical shifts of  $-1.46$  eV and  $-2.50$  eV for Fe $2p_{2/3}$  and Cu $2p_{2/3}$ , respectively, were observed at  $10\text{ g L}^{-1}$  NaCl, compared to the control, suggesting that chemical reduction had occurred on the catalyst surface (De Los Arcos et al. 2002). To sum up, XPS analysis strongly supported the hypothesis that the presence of  $\text{Cl}^-$  promoted the rate of oxidation of phenol by accelerating the rate-limiting step of the decomposition of  $\text{H}_2\text{O}_2$  (the process of activation via the reduction of active metal species on the catalyst surfaces).

Although the changes in the  $\text{Cl}^-$  concentration (Supplementary, Figure S2) and the mass spectra (Supplementary, Figure S3) showed that trace amounts of  $\text{Cl}^-$  directly participated in the oxidation of phenol resulting in chlorination (the formation of 4-CP and other chlorinated intermediates), the extent of chlorination reaction was negligible. Thus, the enhancement in the oxidation rate of phenol by  $\text{Cl}^-$  was not due to chlorination, as proposed by some researchers (Chen & Pignatello 1997; Vione et al. 2005; Du et al. 2006), but due to the promotion of the reduction-decomposition reaction (reaction 3) mentioned above.

## CONCLUSIONS

The oxidation of phenol by  $\text{H}_2\text{O}_2$  over clay-based catalysts with and without NaCl was studied. The results show that the presence of  $\text{Cl}^-$  promoted the oxidation rate of phenol significantly (up to a maximum of 155%) and altered the composition of the dominant organic acids formed during the reaction. However, the presence of  $\text{Cl}^-$  did not significantly influence the deep oxidation of phenol (mineralization). Multiple indicators including such as  $\text{Cl}^-$  concentration, extent of metal leaching,  $\text{H}_2\text{O}_2$  decomposition, and solution pH, in addition to MS and XPS analyses, showed that the presence of  $\text{Cl}^-$  effectively accelerated phenol oxidation and shortened the induction period by promoting the rate-limiting step of  $\text{H}_2\text{O}_2$  decomposition. The results of this study suggest that the CWPO technology is promising for applications in actual saline phenolic wastewater treatment.

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