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

Shiwei Zhou, Changbo Zhang, Rui Xu, Chuantao Gu, Zhengguo Song and Minggang Xu

## ABSTRACT

Catalytic wet peroxide oxidation (CWPO) of phenol over clay-based catalysts in the presence and absence of NaCl was investigated. Changes in the $H_2O_2$, $Cl^-$, 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 $Cl^-$ increased the oxidation rate of phenol to 155%, and this phenomenon was ubiquitous during the oxidation of phenolic compounds by $H_2O_2$ over clay-based catalysts. $Cl^-$-assisted oxidation of phenol was evidenced by several analytical techniques such as mass spectroscopy (MS) and XPS, and it was hypothesized that the rate-limiting step was accelerated in the presence of $Cl^-$. 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

Shiwei Zhou
Minggang Xu (corresponding author)
National Engineering Laboratory for Improving
    Quality of Arable Land,
Institute of Agricultural Resources and Regional
    Planning, Chinese Academy of Agricultural
    Sciences,
Beijing 100081,
China
E-mail: xuminggang@caas.cn

Changbo Zhang
Zhengguo Song
Ministry of Agriculture,
Ago-Environmental Protection Institute,
Tianjin 300191,
China

Rui Xu
Chuantao Gu
Chemistry & Chemical Engineering College,
Yantai University,
Yantai 264005,
China

## 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 (•OH) generated via the catalytic decomposition of $H_2O_2$ 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 none 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 a previous study (Zhou et al. 2011a), 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 a novel observation which deserved further attention, 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 •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), $H_2O_2$, and

$Cl^-$ 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). Furthermore, Micó et al. (2013) attributed the enhancement of $Cl^-$ to the participation of $^\bullet Cl$ in the reaction, whose reaction capacity is comparable with that of $^\bullet OH$. 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 $Cl^-$ exerts a complex effect on the CWPO reaction of phenol, and its mechanism is still unclear.

Herein, the role of $Cl^-$ 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 $Cl^-$ is a ubiquitous phenomenon which still occurs even in high salt (0.17 M NaCl solution); and (2) to reveal the mechanism involved in $Cl^-$-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 ($Cu_{4.8}Ni_{1.2}Al_2$-hydrotalcite, $Cu_6Al_2$-hydrotalcite/clay composite and $Al_5$-$Fe_{0.5}$-$Cu_{0.5}$-pillared clay) were synthesized and characterized in our previous studies (Zhou et al. 2011a, b, 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 $H_2O_2$

Following the method described in the previous studies (Zhou et al. 2011a, b, 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 powder-form were loaded into the flask. The reaction mixture was magnetically stirred and heated to 30 °C, following which $H_2O_2$ (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 $MnO_2$ in order to eliminate residual $H_2O_2$ (Liou & Chen 2009), then filtered and the concentrations of phenol, total organic carbon (TOC), $Cl^-$ and dissolved metals (Fe and Cu) were analyzed; whereas the other portion was directly filtered to determine the residual amount of $H_2O_2$. 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 $CH_2Cl_2$, and then its concentration was determined using an Agilent 7890A GC, following the previous method (Zhou et al. 2011a). Another 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 $Cl^-$ was measured by ion chromatography (Dionex ICS3000); $H_2O_2$ content was analyzed by a spectrophotometric method using ammonium metavanadate (Nogueira et al. 2005). Additionally, solution pH was monitored every 2 s during the 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 $Cl^-$

In a previous study (Zhou et al. 2011a), we found that the presence of $NaNO_3$ markedly decreased the oxidation rate of phenol over Cu-Ni-Al hydrotalcite, whereas the presence of $Cl^-$ 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 $Cl^-$, further supports the results from the previous study. The maximum increase in the rate of oxidation of

**Table 1** │ Influence of inorganic salts on phenol oxidation by $H_2O_2$ over different heterogeneous catalysts (reaction conditions: [phenol] = 2.66 mM; n ($H_2O_2$)/n (phenol) = 15; [catalyst] = 1 g $L^{-1}$; temperature = 30 °C)

| Catalyst[a] | Salt | | | | | |
|---|---|---|---|---|---|---|
| | Type | Concentration (mM) | Time (min) | Conversion (%) | Average rate (mM $min^{-1}$) | Increase rate (%) |
| A | Control | 0 | 90 | 100 | $2.95 \times 10^{-2}$ | – |
| | NaCl | 17.11 | 60 | 100 | $4.42 \times 10^{-2}$ | 49.8 |
| | NaCl | 102.66 | 40 | 100 | $6.64 \times 10^{-2}$ | 125.1 |
| | KCl | 13.41 | 60 | 94.4 | $4.18 \times 10^{-2}$ | 41.7 |
| | $NH_4Cl$ | 18.69 | 90 | 100 | $2.95 \times 10^{-2}$ | 0 |
| | $CaCl_2$ | 9.01 | 60 | 100 | $4.42 \times 10^{-2}$ | 49.8 |
| | $MgCl_2$ | 10.50 | 60 | 98.9 | $4.38 \times 10^{-2}$ | 48.5 |
| | NaBr | 9.72 | 120 | 19.8 | $4.39 \times 10^{-3}$ | −85.1 |
| | $NaNO_3$ | 11.77 | 120 | 41.3 | $9.14 \times 10^{-3}$ | −69.0 |
| B | Control | 0 | 90 | 99.2 | $2.93 \times 10^{-2}$ | – |
| | NaCl | 8.56 | 60 | 91.4 | $4.05 \times 10^{-2}$ | 38.2 |
| | NaCl | 17.11 | 60 | 97.8 | $4.33 \times 10^{-2}$ | 47.8 |
| | KCl | 13.41 | 60 | 93.8 | $4.16 \times 10^{-2}$ | 41.9 |
| | $NH_4Cl$ | 18.69 | 90 | 99.0 | $2.93 \times 10^{-2}$ | 0 |
| | $NH_4Cl$ | 28.04 | 60 | 95.0 | $4.21 \times 10^{-2}$ | 43.7 |
| | $CaCl_2$ | 9.01 | 60 | 100 | $4.42 \times 10^{-2}$ | 50.9 |
| | $MgCl_2$ | 10.50 | 60 | 75.8 | $3.36 \times 10^{-2}$ | 14.6 |
| | NaBr | 9.72 | 120 | 18.8 | $4.16 \times 10^{-3}$ | −85.8 |
| C | Control | 0 | 55 | 27.0 | $1.31 \times 10^{-2}$ | – |
| | NaCl | 17.11 | 55 | 34.7 | $1.68 \times 10^{-2}$ | 28.2 |
| | NaCl | 171.11 | 55 | 69.1 | $3.34 \times 10^{-2}$ | 155.0 |
| | NaBr | 9.72 | 120 | 18.1 | $4.01 \times 10^{-3}$ | −69.3 |

[a]A: $Cu_{4.8}Ni_{1.2}Al_2$-hydrotalcite; B: $Cu_6Al_2$-hydrotalcite/clay composite; C: $Al_5$-$Fe_{0.5}$-$Cu_{0.5}$-pillared clay (500).

phenol was 155% in the presence of 10 g $L^{-1}$ (0.17 M) of NaCl, whereas the oxidation rate decreased greatly in the presence of NaBr and $NaNO_3$. These results have significant implications for the possible application of the CWPO technology in phenolic wastewater treatment, considering the high $Cl^-$ 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 tri-chlorophenols (MCPs, DCPs and TCPs, respectively) were found to undergo $Cl^-$-assisted oxidation over the clay-based catalyst considered in this study (Table 2). $Cl^-$-assisted oxidation appears to be a novel and ubiquitous phenomenon, in particular $Cl^-$-assisted oxidation of CPs has never been observed previously, because it is widely accepted that $Cl^-$ inhibits Fenton-like processes by scavenging •OH or by competing with $H_2O_2$ for the complexation of Fe(III) (De Laat & Le 2006; Pignatello *et al.* 2006), and even the inhibitory effect is noticeable only at $Cl^-$ 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 $L^{-1}$ of NaCl (0.17 M $Cl^-$), which is a much higher concentration, phenol oxidation is in fact promoted, and moreover, the rates of phenol oxidation

increased obviously with increasing $Cl^-$ concentration (Table 1). Therefore, $Cl^-$ 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 $Cl^-$ 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). Furthermore, it is observed from Figure 1 that concentration of $Cl^-$ 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 $L^{-1}$ 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 with acrylic acid. However, no difference was observed in the final TOC conversion (%) in the presence and absence of NaCl (Supplementary Material, Figure S1, available with the online version of this paper), suggesting

**Table 2** | The oxidation of chlorophenols (CPs) by $H_2O_2$ over $Cu_6Al_2$-hydrotalcite/clay composite in the absence and presence of NaCl (reaction conditions: [CP] = 2 mM; n ($H_2O_2$)/n (CP) = 20; [catalyst] = 1.0 g $L^{-1}$; [NaCl] = 1 g $L^{-1}$; temperature = 40 °C)
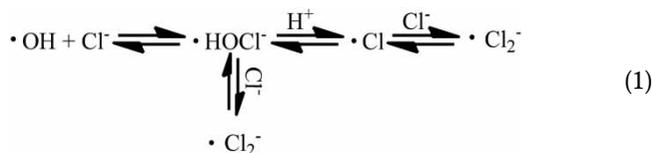
| Chlorophenol (CP) | NaCl | Time (min) | Average rate (mM $min^{-1}$) | Increase rate (%) |
|---|---|---|---|---|
| 3-CP | Without | 10 | $1.02 \times 10^{-1}$ | – |
| 3-CP | With | 10 | $1.64 \times 10^{-1}$ | 60.8 |
| 2-CP | Without | 20 | $6.53 \times 10^{-2}$ | – |
| 2-CP | With | 20 | $8.83 \times 10^{-2}$ | 35.2 |
| 4-CP | Without | 30 | $5.07 \times 10^{-2}$ | – |
| 4-CP | With | 30 | $5.91 \times 10^{-2}$ | 16.6 |
| 3,4-DCP | Without | 30 | $4.39 \times 10^{-2}$ | – |
| 3,4-DCP | With | 30 | $6.23 \times 10^{-2}$ | 41.9 |
| 3,5-DCP | Without | 20 | $4.86 \times 10^{-2}$ | – |
| 3,5-DCP | With | 20 | $8.86 \times 10^{-2}$ | 82.3 |
| 2,5-DCP | Without | 30 | $2.56 \times 10^{-2}$ | – |
| 2,5-DCP | With | 30 | $5.41 \times 10^{-2}$ | 111.3 |
| 2,4-DCP | Without | 90 | $1.74 \times 10^{-2}$ | – |
| 2,4-DCP | With | 90 | $2.07 \times 10^{-2}$ | 19.0 |
| 2,6-DCP | Without | 180 | $8.98 \times 10^{-3}$ | – |
| 2,6-DCP | With | 180 | $9.05 \times 10^{-3}$ | 0.8 |
| 2,4,6-TCP | Without | 300 | $5.58 \times 10^{-3}$ | – |
| 2,4,6-TCP | With | 300 | $5.95 \times 10^{-3}$ | 6.6 |

that $Cl^-$ only played a major role in increasing the oxidation rate of phenol (conversion), and did not significantly influence its deep oxidation (mineralization).

The above discussion on the role of $Cl^-$ suggests that the presence of $Cl^-$ 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 photodegradation due to the formation of high active chlorine

and radicals besides $^\bullet OH$ (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 $NH_4Cl$ results are not closer with respect to the rest, the reason for which is not clear. What is more important is that $NH_4^+$ and $NO_3^-$ are also present in actual saline wastewater, which would undoubtedly weaken the effect of $Cl^-$. Maybe this technology should be tried first 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 $^\bullet Cl$ in the reaction, since the rate constants for the reactions of organic compounds with $^\bullet Cl$ were comparable with those with $^\bullet OH$. However, it was almost impossible to generate $^\bullet Cl$ in reaction systems near neutral pH in view of reaction (1) (Pignatello *et al.* 2006), which involves not only the consumption of $^\bullet OH$, but also the formation of less reactive $^\bullet Cl_2^-$.

$$\cdot OH + Cl^- \rightleftharpoons \cdot HOCl^- \xrightarrow[]{H^+} \cdot Cl \overset{Cl^-}{\rightleftharpoons} \cdot Cl_2^- \qquad \downarrow Cl^- \qquad \cdot Cl_2^- \tag{1}$$

## Mechanism of the enhancement of phenol oxidation rate by $Cl^-$

Figure 2 illustrates the interdependence among $H_2O_2$ 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
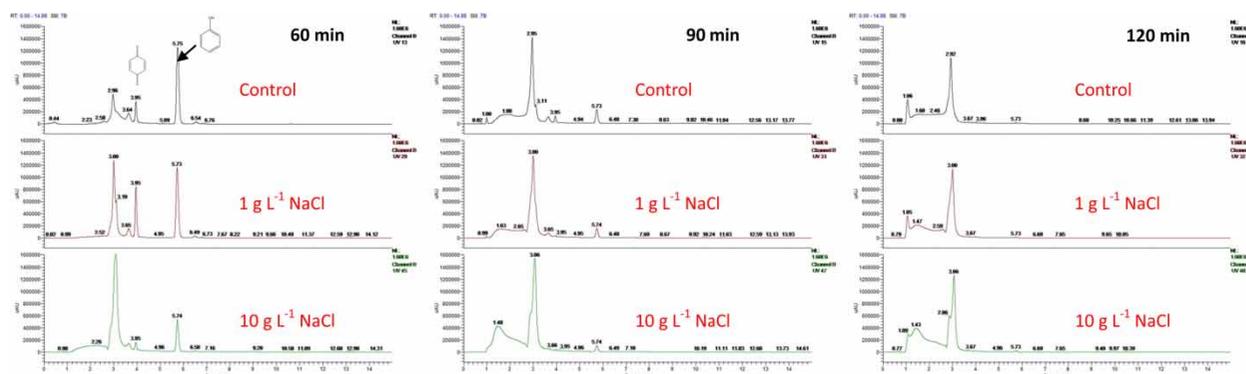


**Figure 1** | Chromatograms of LC-MS for phenol oxidation by $H_2O_2$ over $Al_5$-$Fe_{0.5}$-$Cu_{0.5}$-PILC (500) under different NaCl addition after 60 min (left), 90 min (middle) and 120 min (right) (reaction conditions: [phenol] = 2.66 mM; [$H_2O_2$] = 40 mM; [catalyst] = 1 g $L^{-1}$; temperature = 30 °C).

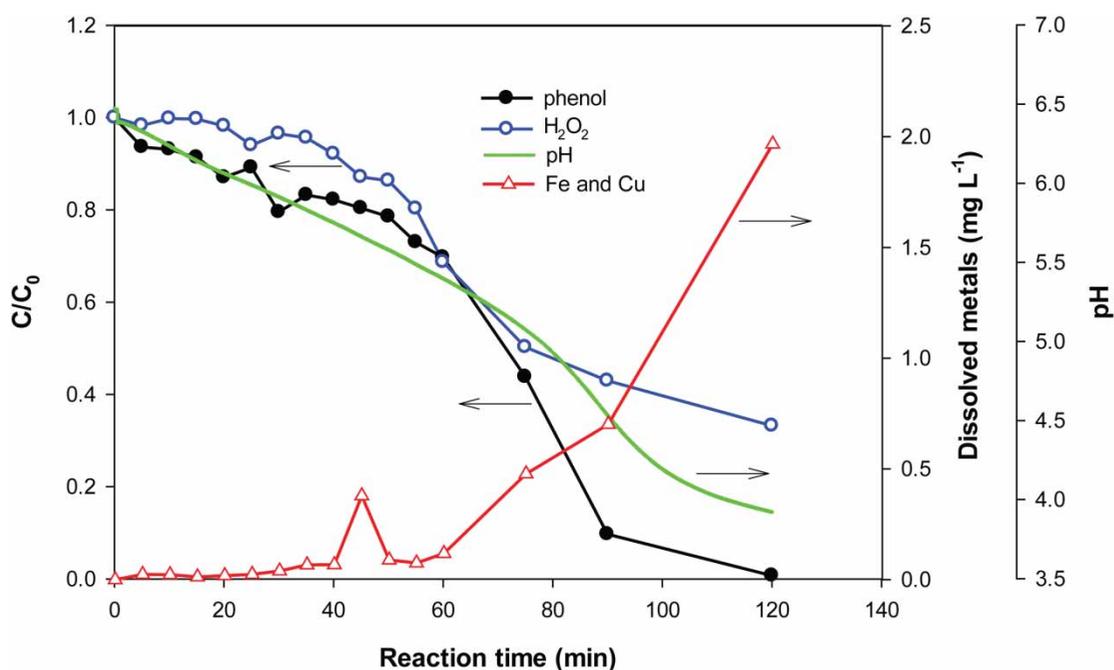**Figure 2** | Kinetic profiles of H$_2$O$_2$ decomposition, metallic dissolution and pH changes during catalytic reaction of phenol over Al$_5$-Fe$_{0.5}$-Cu$_{0.5}$-PILC (500) (reaction conditions: [phenol] = 2.66 mM; [H$_2$O$_2$] = 40 mM; [catalyst] = 1 g L$^{-1}$; temperature = 30 °C).

shown in Figure 2 suggest that the decrease in pH caused 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$^{-1}$) 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):

$$\equiv Fe^{III} + H_2O_2 \rightarrow \equiv Fe^{III}H_2O_2 \tag{2}$$

$$\equiv Fe^{III}H_2O_2 \rightarrow \equiv Fe^{II} + \bullet HO_2 + H^+ \tag{3}$$

$$\equiv Fe^{II} + H_2O_2 \rightarrow \equiv Fe^{III} + \bullet OH + OH^- \tag{4}$$

Timofeeva *et al.* (2005) confirmed the formation of peroxide-Fe$^{3+}$ complexes upon the interaction of H$_2$O$_2$ and Al-Fe-PILC, by electron spin resonance (ESR) and diffuse reflectance UV-visible (DR-UV-Vis) spectra. It was also assumed that reaction (3), where the pH is lower as a result
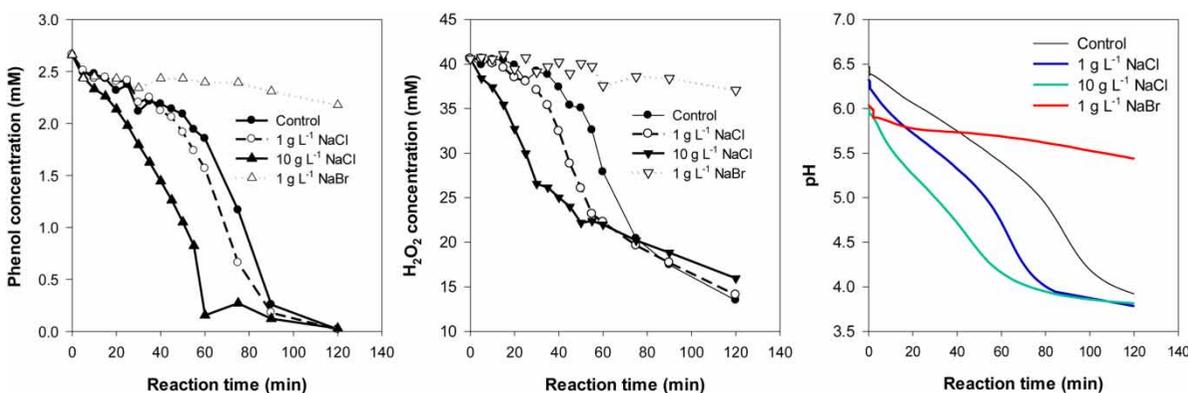


**Figure 3** | Profiles of phenol oxidation, H$_2$O$_2$ decomposition and pH change during catalytic reaction of phenol over Al$_5$-Fe$_{0.5}$-Cu$_{0.5}$-PILC (500) under different NaCl addition (reaction conditions: [phenol] = 2.66 mM; [H$_2$O$_2$] = 40 mM; [catalyst] = 1 g L$^{-1}$; temperature = 30 °C).

**Table 3** | The content (atom %) of main elements and atomic ratios (O/Fe, C/Fe and Cl/Fe) of Al$_5$-Fe$_{0.5}$-Cu$_{0.5}$-PILC (500) measured by XPS before and after catalytic oxidation of phenol by H$_2$O$_2$ 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$^{-1}$ NaCl | 49.86 | 17.24 | 11.54 | 12.82 | 1.48 | 1.42 | – | 33.67 | 8.66 | 0.96 |
| 10 g L$^{-1}$ NaCl | 35.79 | 10.60 | 6.95 | 25.90 | 1.47 | 4.19 | 4.34 | 24.32 | 17.60 | 2.85 |

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$_2$O$_2$ 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$_2$O$_2$ and the subsequent reduction-

decomposition of the complexes. In addition, the lower pH, the shorter the induction time would be. In short, at the initial stage of the catalytic reaction (induction period), the pH decreased monotonously during the adsorption and subsequent decomposition of H$_2$O$_2$, 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$_2$O$_2$ decomposition, and pH decrease were observed to exhibit a highly consistent
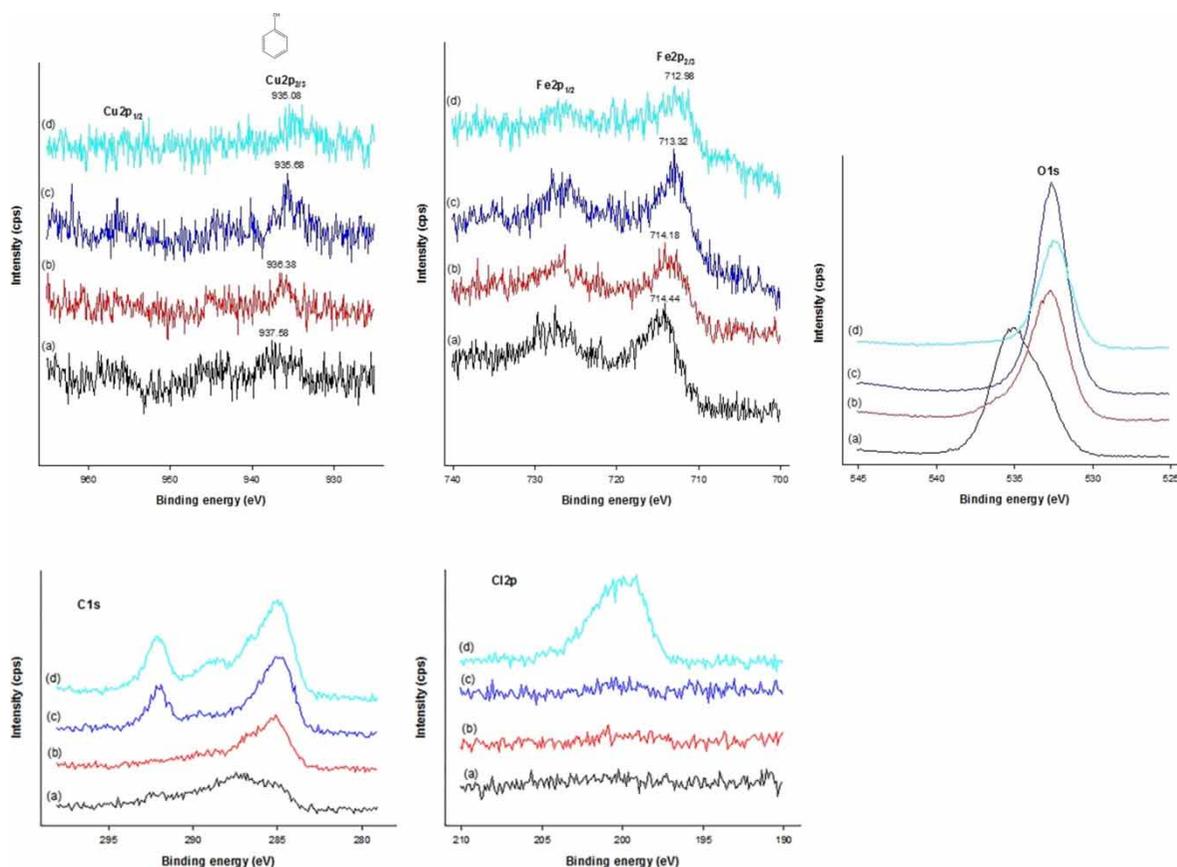


**Figure 4** | XPS spectra of Cu2p, Fe2p, O1s, C1s and Cl2p spectral regions of Al$_5$-Fe$_{0.5}$-Cu$_{0.5}$-PILC (500) before and after catalytic oxidation of phenol by H$_2$O$_2$ with and without NaCl: (a) control before reaction; (b) control after reaction; (c) 1 g L$^{-1}$ NaCl; and (d) 10 g L$^{-1}$ NaCl.

relationship in the presence and absence of NaCl (Figure 3). In other words, compared with the control sample (without NaCl), faster decomposition of $H_2O_2$ 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 $Cl^-$ promoted the rate of oxidation of phenol by accelerating the rate-limiting step of the surface-catalyzed decomposition of $H_2O_2$ (reaction (3)).

Further, the O/Fe atomic ratio decreased markedly by 13.5 in the presence of $10\,g\,L^{-1}$ of NaCl compared with the control (Table 3), indicating a more reductive environment for the degradation of phenol. Additionally, in the XPS spectra of the catalyst surface, apparent chemical shifts to lower binding energies were observed in Figure 4 in the presence of NaCl. Chemical shifts of $-1.46\,eV$ and $-2.50\,eV$ for $Fe2p_{2/3}$ and $Cu2p_{2/3}$, respectively, were observed at $10\,g\,L^{-1}$ NaCl, compared with 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 $Cl^-$ promoted the rate of oxidation of phenol by accelerating the rate-limiting step of the decomposition of $H_2O_2$ (the process of activation via the reduction of active metal species on the catalyst surfaces).

Although the changes in the $Cl^-$ concentration (Supplementary Material, Figure S2) and the mass spectra (Supplementary Material, Figure S3) (Supplementary Material is available with the online version of this paper) showed that trace amounts of $Cl^-$ 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 $Cl^-$ 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 $H_2O_2$ over clay-based catalysts with and without NaCl was studied. The results show that the presence of $Cl^-$ 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 $Cl^-$ did not significantly influence the deep oxidation of phenol

(mineralization). Multiple indicators including such as $Cl^-$ concentration, extent of metal leaching, $H_2O_2$ decomposition, and solution pH, in addition to MS and XPS analyses, showed that the presence of $Cl^-$ effectively accelerated phenol oxidation and shortened the induction period by promoting the rate-limiting step of $H_2O_2$ decomposition. The results of this study suggest that the CWPO technology is promising for applications in actual saline phenolic wastewater treatment.

## REFERENCES

Belaroui, L. S. & Bengueddach, A. 2012 Study of the catalytic activity of Al-Fe pillared clays in the Baeyer-Villiger oxidation. *Clay Minerals* **47**, 275–284.

Chen, R. Z. & Pignatello, J. J. 1997 Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. *Environmental Science & Technology* **31**, 2399–2406.

De Laat, J. & Le, T. G. 2006 Effects of chloride ions on the iron (III)-catalyzed decomposition of hydrogen peroxide and on the efficiency of the Fenton-like oxidation process. *Applied Catalysis B-Environmental* **66**, 137–146.

De Laat, J., Le, T. G. & Legube, B. 2004 A comparative study of the effects of chloride, sulfate and nitrate ions on the rates of decomposition of $H_2O_2$ and organic compounds by Fe(II)/ $H_2O_2$ and Fe(III)/$H_2O_2$. *Chemosphere* **55**, 715–723.

De Los Arcos, T., Vonau, F., Garnier, M. G., Thommen, V., Boyen, H. G., Oelhafen, P., Düggelin, M., Mathis, D. & Guggenheim, R. 2002 Influence of iron-silicon interaction on the growth of carbon nanotubes produced by chemical vapor deposition. *Applied Physics Letters* **80**, 2383–2385.

Du, Y. X., Zhou, M. H. & Lei, L. C. 2006 Role of the intermediates in the degradation of phenolic compounds by Fenton-like process. *Journal of Hazardous Materials* **B136**, 859–865.

Galeano, L. A., Vicente, M. A. & Gil, A. 2014 Catalytic degradation of organic pollutants in aqueous streams by mixed Al/M-pillared clays (M = Fe, Cu, Mn). *Catalysis Reviews-Science and Engineering* **56**, 239–287.

Garrido-Ramírez, E. G., Theng, B. K. G. & Mora, M. L. 2010 Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions–A review. *Applied Clay Science* **47**, 182–192.

Huang, C. P. & Huang, Y. H. 2008 Comparison of catalytic decomposition of hydrogen peroxide and catalytic degradation of phenol by immobilized iron oxides. *Applied Catalysis A-General* **346**, 140–148.

Kurian, M. & Sugunan, S. 2006 Wet peroxide oxidation of phenol over mixed pillared montmorillonites. *Chemical Engineering Journal* **115**, 139–146.

Kwan, W. P. & Voelker, B. M. 2003 Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems. *Environmental Science & Technology* **37**, 1150–1158.

Liotta, L. F., Gruttadauria, M., Di Carlo, G., Perrini, G. & Librando, V. 2009 Heterogeneous catalytic degradation of phenolic substrates: catalysts activity. *Journal of Hazardous Materials* **162**, 588–606.

Liou, R. M. & Chen, S. H. 2009 Cuo impregnated activated carbon for catalytic wet peroxide oxidation of phenol. *Journal of Hazardous Materials* **172**, 498–506.

Machulek, A., Moraes, J. E. F., Vautier-Giongo, C., Silverio, C. A., Friedrich, L. C., Nascimento, C. A. O., Gonzalez, M. C. & Quina, F. H. 2007 Abatement of the inhibitory effect of chloride anions on the photo-fenton process. *Environmental Science & Technology* **41**, 8459–8463.

Mahamuni, N. N. & Pandit, A. B. 2006 Effect of additives on ultrasonic degradation of phenol. *Ultrasonics Sonochemistry* **13**, 165–174.

Micó, M. M., Bacardit, J., Malfeito, J. & Sans, C. 2013 Enhancement of pesticide photo-Fenton oxidation at high salinities. *Applied Catalysis B-Environmental* **132–133**, 162–169.

Nogueira, R. F. P., Oliveira, M. C. & Paterlini, W. C. 2005 Simple and fast spectrophotometric determination of $H_2O_2$ in photo-Fenton reactions using metavanadate. *Talanta* **66**, 86–91.

Pignatello, J. J., Oliveros, E. & MacKay, A. 2006 Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology* **36**, 1–84.

Rokhina, E. V. & Virkutyte, J. 2011 Environmental application of catalytic processes: heterogeneous liquid phase oxidation of phenol with hydrogen peroxide. *Critical Reviews in Environmental Science and Technology* **41**, 125–167.

Tatibouët, J. M., Guélou, E. & Fournier, J. 2005 Catalytic oxidation of phenol by hydrogen peroxide over a pillared clay containing iron. Active species and pH effect. *Topics in Catalysis* **33**, 225–232.

Timofeeva, M. N., Khankhasaeva, S. T., Badmaeva, S. V., Chuvilin, A. L., Burgina, E. B., Ayupov, A. B., Panchenko, V. N. & Kulikova, A. V. 2005 Synthesis, characterization and catalytic application for wet oxidation of phenol of iron-containing clays. *Applied Catalysis B-Environmental* **59**, 243–248.

Vione, D., Maurino, V., Minero, C., Calza, P. & Pelizzetti, E. 2005 Phenol chlorination and photochlorination in the presence of chloride ions in homogeneous aqueous solution. *Environmental Science & Technology* **39**, 5066–5075.

Xiao, S. H., Song, Y. H., Tian, Z. Y., Tu, X., Hu, X. Q. & Liu, R. X. 2015 Enhanced mineralization of antibiotic berberine by the photoelectrochemical process in presence of chlorides and its optimization by response surface methodology. *Environmental Earth Sciences* **73**, 4947–4955.

Zhou, S. W., Qian, Z. Y., Sun, T., Xu, J. G. & Xia, C. H. 2011a Catalytic wet peroxide oxidation of phenol over Cu-Ni-Al hydrotalcite. *Applied Clay Science* **53**, 627–633.

Zhou, S. W., Gu, C. T., Qian, Z. Y., Xu, J. G. & Xia, C. H. 2011b The activity and selectivity of catalytic peroxide oxidation of chlorophenols over Cu-Al hydrotalcite/clay composite. *Journal of Colloid and Interface Science* **357**, 447–452.

Zhou, S. W., Zhang, C. B., Hu, X. F., Wang, Y. H., Xu, R., Xia, C. H., Zhang, H. & Song, Z. G. 2014 Catalytic wet peroxide oxidation of 4-chlorophenol over Al-Fe-, Al-Cu-, and Al-Fe-Cu-pillared clays: Sensitivity, kinetics and mechanism. *Applied Clay Science* **95**, 275–283.

Zhou, Y. B., Gu, X. C., Zhang, R. Z. & Lu, J. 2015 Influences of various cyclodextrins on the photodegradation of phenol and bisphenol A under UV light. *Industrial & Engineering Chemistry Research* **54**, 426–433.