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Comparison treatment of various chlorophenols by electro-Fenton method: relationship between chlorine content and degradation

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Abstract

This study describes a comparative degradation of various chlorophenols by electro-Fenton method. Chloride released and reaction intermediate products were determined by ionic chromatography (IC) and gas chromatography/mass spectrometry (GC/MS). Using pentachlorophenol (PCP) as the model compound, we investigated the effects of cell voltage, electrolyte concentration and pH to optimize the degradation conditions. It was noted that the addition of small quantities of Fe^{3+} or Fe^{2+} significantly accelerated the degradation rate. Under the optimal conditions, electro-Fenton method was used to treat various chlorophenols including PCP, 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and their mixture aqueous solutions. Their pseudo first-order degradation rate constants at the first stages were calculated and compared, which gave the following sequence: 2,4-DCP > 2,4,6-TCP > PCP > 4-CP. The relationship between the chlorine content and degradation rate was discussed and compared with other advanced oxidation processes. Finally, we proposed the degradation pathways of different chlorophenols.

1. Introduction

Within the last decade, there has been a growing concern related to environmental and health impacts of chlorinated organic compounds. Chlorophenols constitute a group of organic substances that were introduced into the environment from several man-made activities, such as wood preservatives, waste incineration, uncontrolled use of pesticides, fungicides and herbicides, as well as by-products formed during bleaching of pulp with chlorine and in chlorination disinfection of drinking water [1]. As they are harmful to human health, several of them have been listed among the 65 priority pollutants by the US EPA [2]. Therefore, it was of great importance to develop effective methods to remove them from water.

Because of their toxic nature to microorganism, conventional biological methods are not suitable for their removal. Advanced oxidation processes (AOPs) such as Fenton's reagent, ozone, UV, UV/H_2O_2, UV/Fenton, and ultrasound were studied [3–10]. Photolysis or ultrasound alone was not effective, while photocatalysis or assisted photochemistry need additional reagent like H_2O_2 or TiO_2. And it is the same for assisted sonolysis. Recently, a new advanced oxidation process induced by electrochemistry was proposed as an alternative process. Fenton's reagent may be produced in the bulk solution. Electro-Fenton approach consisted of either adding ferrous iron or reducing ferric iron electrochemically with the simultaneous production of hydrogen peroxide upon the reduction of oxygen on several electrodes (mercury pool, vitreous carbon or carbon-polytetrafluoroethylene O_2-fed cathodes) [11–17].

Degradation kinetics with various chlorophenols had been compared by Fenton's reagent [18,19], photolysis [20,21], O_3 [5], sonolysis [22] and different degradation sequences were

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provided. However, there was no report using electro-Fenton method to treat various chlorophenols. In this study, 4-CP, 2,4-DCP, 2,4,6-TCP and PCP were degraded with electro-Fenton method. A special attention was paid to the relationship between chlorine content and degradation rate. Finally, the reaction pathways of different chlorophenols were proposed.

2. Materials and methods

2.1. Chemicals and materials

PCP (C.P. Grade) was obtained from Qingpu Synthetical Reagent Factory, Shanghai, China. Standard materials of 4-CP and 2,4-DCP were obtained from Sigma, and 2,4,6-TCP from PA. Tetrachloro-*p*-hydroquinone and tetrachloro-*o*-hydroquinone (both standard material) were commercially available from Acros. $FeSO_4$ and $Fe_2(SO_4)_3$ (both A.R. Grade) were used as the sources of ferrous and ferric ion, respectively. Trichloromethane (A.R. Grade) was used in liquid–liquid extraction procedures. Deionized water (18.2 mΩ) obtained from a Millipore Milli-Q system was used for the preparation of synthetic wastewater and the other solutions. All the other reagents used were above A.R. grade. A graphite stick (Φ 25 mm $\times$ 90 mm) and a platinum piece (5 mm $\times$ 5 mm) were used as cathode and anode, respectively. SCE reference electrode was also employed.

2.2. Procedures and equipment

Electrochemical experiments were carried out with an undivided glass cell of 250 mL capacity containing the above-stated graphite cathode and platinum anode. An SCE reference electrode was placed in the bulk. Firstly, the cell was filled with 200 mL PCP aqueous solution (16 mg/L), diluted from the stock solution of 1000 mg/L PCP prepared in alkaline aqueous. H_2SO_4 (1.0 mol/L) was added to acidified pH to 2.5 and Na_2SO_4 was added to enhance the conductivity. The cell voltage was provided with a laboratory dc power supply (GPC-3060D). Stirring was applied to the solution using a magnetic stirrer (GPS-77-03). Then, $FeSO_4$ or $Fe_2(SO_4)_3$ was added to study their effects on degradation except for the optimization experiments. Finally, PCP, 4-CP, 2,4-DCP, 2,4,6-TCP and their mixture aqueous solutions were treated under the optimal conditions. All experiments were performed at room temperature.

2.3. Analysis of the samples

The samples (5 mL) were taken out at regular time interval and were adjusted to pH > 7 with NaOH (1.0 mol/L) immediately to terminate further reaction and kept in refrigerator (4 °C) until analysis within 8 h. The samples were centrifuged (6000 rpm) before analysis.

PCP, 4-CP, 2,4-DCP, 2,4,6-TCP were analyzed by reverse-phase chromatography using a high performance liquid chromatography (HPLC) system (Hitachi pumps L-7100 and Hitachi Dynamic mixer) equipped with a UV–vis detector L-7420 and a reverse-phase Hypersil C-18 column (250 mm $\times$ 4.6 mm i.d., 5 mm). The mobile phase was a mixture of 1% acetate acid aqueous solution and methanol with ratios of 75:25 (v/v) for 4-CP and 80:20 (v/v) for the other chlorophenols, respectively. The flow rate of the mobile phase was 1.0 mL/min. Detection was carried out at 278 nm for 4-CP and 295 nm for the other chlorophenols, respectively. Calibration curves were drawn for the quantitative analysis of chlorophenols. The volume of injection was 20 μL.

The concentration of chloride ions released during electrolysis was measured by ionic chromatography (IC, Dionex 120 equipped with a conductivity detector), on a 4-mm anionic exchanger column (IonPack AS4A-SC-Dionex). The volume of injection was 25 μL and the mobile phase was a mixture of 0.94 mmol/L sodium carbonate and 0.83 mmol/L sodium hydrogen carbonate solution with a flow rate of 0.73 ml/min. These conditions were chosen for the reason of interfering of large quantities of SO_4^{2-}.

Typically a 10 mL sample containing chlorophenols and reaction intermediates was acidified to pH < 2 with H_2SO_4 (1.0 mol/L). Then it was extracted twice with chloroform 30 mL each time. The combined extract was dried with sodium sulfate and concentrated to 1 mL by evaporation in water bath (80 °C). The extract was stored at 4 °C until analysis within 8 h.

Identification of intermediates was performed using a gas chromatography (GC, Varian 3900) with a capillary column (FactorFour[TM]: VF-5 ms, 30 m $\times$ 0.25 mm, 0.25 um) and a mass spectrometer (MS, Saturn 2100T), which were programmed with the Saturn Chemstation software (Saturn WS). A split ratio of 15:1, solvent delay at 3 min, and scan range form *m/z* 50 to 500 at 3 s can(s) were used. The oven temperature was programmed from 50 (1 min) to 300 (1 min) at a ramp rate of 8 °C/min. The injection volume of extract was 1 μL. The Nist library was used for tentative species identification as a supplement to mass spectral and retention time characteristics. All library-matched species exhibited the degree of match better than 60%. In addition, comparison of parent compound structure and interpretation of mass spectra of the intermediates from ion fragmentation information were performed particularly for the identification of some key intermediates.
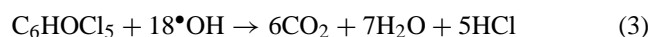
3. Results and discussion

3.1. Optimization of electrolysis
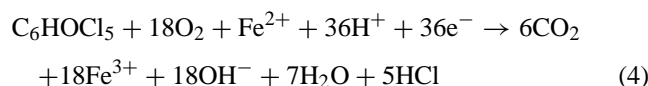
3.1.1. Preliminary experiments

For the electro-Fenton method enough O_2 was necessary for production of H_2O_2. So, an aeration experiment was carried to investigate whether PCP could be blow away during

the process. The results showed that under the same conditions without electricity 60 min aeration (40 mL/min) alone can reduce PCP from 10 mg/L to 5.45 mg/L. So aeration should be avoided in the process in order to prevent vaporization of PCP.

In the electro-Fenton process, the related reactions of PCP degradation are as follows:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{2}$$

$$C_6HOCl_5 + 18^{\bullet}OH \rightarrow 6CO_2 + 7H_2O + 5HCl \tag{3}$$

The combination of (1)–(3) was:

$$C_6HOCl_5 + 18O_2 + Fe^{2+} + 36H^+ + 36e^- \rightarrow 6CO_2$$
$$+ 18Fe^{3+} + 18OH^- + 7H_2O + 5HCl \tag{4}$$

According to the above equation, in order to produce 16 mg/L PCP, 34.56 mg/L O_2 was needed. This value is quite above the intrinsic solubility of O_2 at room temperature (8–9 mg/L). So, O_2 needs be constantly generated in the bulk by electrolysis of water.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{5}$$

Assumed that the dissolved O_2 before electrolysis was 0 mg/L, to obtain 34.56 mg/L dissolved O_2, the theoretical coulomb was 43.36 C. When 50 mA was used, assuming 100% current efficiency [12], 14.45 min were required, which meant that O_2 in the bulk was enough with 120 min electrolysis.

After ferrous or ferric was added to the system, some precipitation was formed when the sample was adjusted to pH > 7. In order to verify the effect of precipitation on the concentration of PCP, a control precipitation experiment was carried out. The results indicated that the concentration was almost constant after precipitation treatment. So the effect of precipitation on the PCP change could be neglected in the process of sample treatment before analysis.

3.1.2. Optimization experiments

The optimization experiments were carried out with different conditions. Fig. 1 gives the results.

It can be seen from Fig. 1(a) that the voltage had no obvious influence on the degradation. The average values of the current determined were about 0.02, 0.06 and 0.13 A corresponding to 3, 5 and 7.5 V, respectively. The measurement of electrode potentials showed that cathode potential and anode potential were −0.55 and 2.95 V (SCE), respectively, in 5 V voltage. Both electrode potentials were beneficial to O_2 reduction to H_2O_2 on graphite cathode and SO_4^{2-} oxidation to $S_2O_8^{2-}$ on Pt anode, which could oxidize H_2O to H_2O_2 [12,22,26]. The influence of low voltage may originate from the dechlorination of PCP on cathode and oxidation on Pt anode directly [30], while at high voltage the competitive
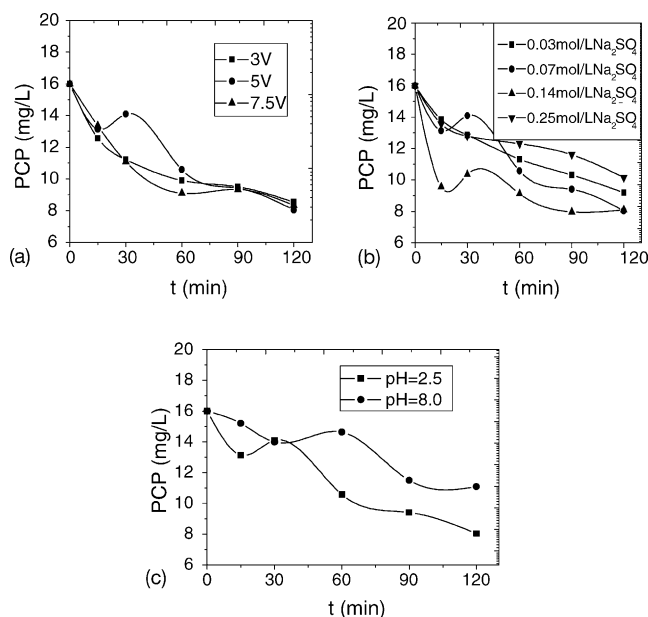

Fig. 1. Optimization of electrolysis. (a) Influence of cell voltage, 0.14 mol/L Na_2SO_4, pH = 2.5; (b) influence of electrolyte concentration, 5 V cell voltage, pH = 2.5; (c) influence of pH, 5 V cell voltage, 0.14 mol/L Na_2SO_4.

electrode reactions such as the discharge of O_2 ($E^0 = 0.988$ V (SCE)) and H_2 ($E^0 = -0.241$ V (SCE)) inhibit main reactions.

Large quantities of electrolyte could enhance the conductivity and provide high current density. Saracco [26,27] studied the effect of quantities of Na_2SO_4 on the coumaric acid degradation on Pt–Ti anode, which verified that more electrolyte could contribute to more H_2O_2 generation resulted from the generation of $S_2O_8^{2-}$. However, it was also reported that the electrogenerated H_2O_2 could be oxidized to O_2 at the anode to give $HO_2^{\bullet}$ as an intermediate, a radical much less oxidant than $^{\bullet}OH$ [28]. Therefore, the reasons that no beneficial effect was observed at high electrolyte concentration could be interpreted as follows. The reactions of H_2O_2 and PCP without catalyst were not easy to take place, and H_2O_2 would be oxidized to produce O_2 when the electrolyte quantity became enough to generate H_2O_2 [28]. Another possible explanation is the low ability of pure Pt anode alone to generate $S_2O_8^{2-}$ because of surface oxidation in acidic aqueous [23].

Fig. 1(c) shows that in acidic conditions the degradation of PCP is faster. PCP is a weak acid (pKa = 4.35), acidic species and anionic species of PCP are the dominant speciation at pH = 2.5 and 8.0, respectively. After dissociation, the density of electron in benzene ring of PCP becomes higher, the electrophilic attack of hydroxyl could happen more easily [24]. However, this phenomenon was not observed in our study, which indicated that the degradation of PCP may not be carried out only by hydroxyl radical. This can be explained by different oxidation abilities of H_2O_2 at different pH, for example, standard oxidation–reduction potential of 1.77 V (SHE) in acidic solution and 0.88 V (SHE) in basic solution. Additionally, it is much easier to produce $HO_2^{\bullet}$ and O_2 in
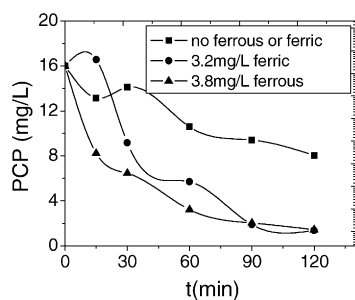
Fig. 2. The influences of the introduction of ferrous and ferric. Conditions: 5 V voltage, 0.14 mol/L NaSO$_4$ electrolyte, pH = 2.5.

basic aqueous than in acidic aqueous [28]. In order to form electro-Fenton system, 2.5 of pH was used in this study [25].

Based on the results, the optimal conditions could be concluded as 5 V of electrolysis voltage, 0.14 mol/L of electrolyte and 2.5 of pH. The conditions were used in all the followed experiments.

3.2. Formation of Fenton's reagent

Under the optimal conditions, ferrous (3.8 mg/L) and ferric (3.2 mg/L) were introduced to the system to observe their influences and to confirm the presence of H$_2$O$_2$ [28].

An obvious acceleration effect was observed in the experiment, as can be seen from Fig. 2. When ferric was added, reaction of (6) may happen on cathode, the generation of ferrous can induce the chain reaction of Fenton's reagent [25].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (6)$$

Because of the time consuming of the reduction of ferric to ferrous and the combination of H$_2$O$_2$ with ferrous ion [31], the degradation of PCP in the initial stage was very slow in case of the ferric addition. When ferrous was generated, hydroxyl radicals could be formed by reaction (2) and accelerate the degradation. It is thought that the regeneration of ferrous here is much easier than conventional Fenton's reaction [25]. Therefore, it is easy to understand that the introduction of ferrous could accelerate the degradation of PCP at the beginning
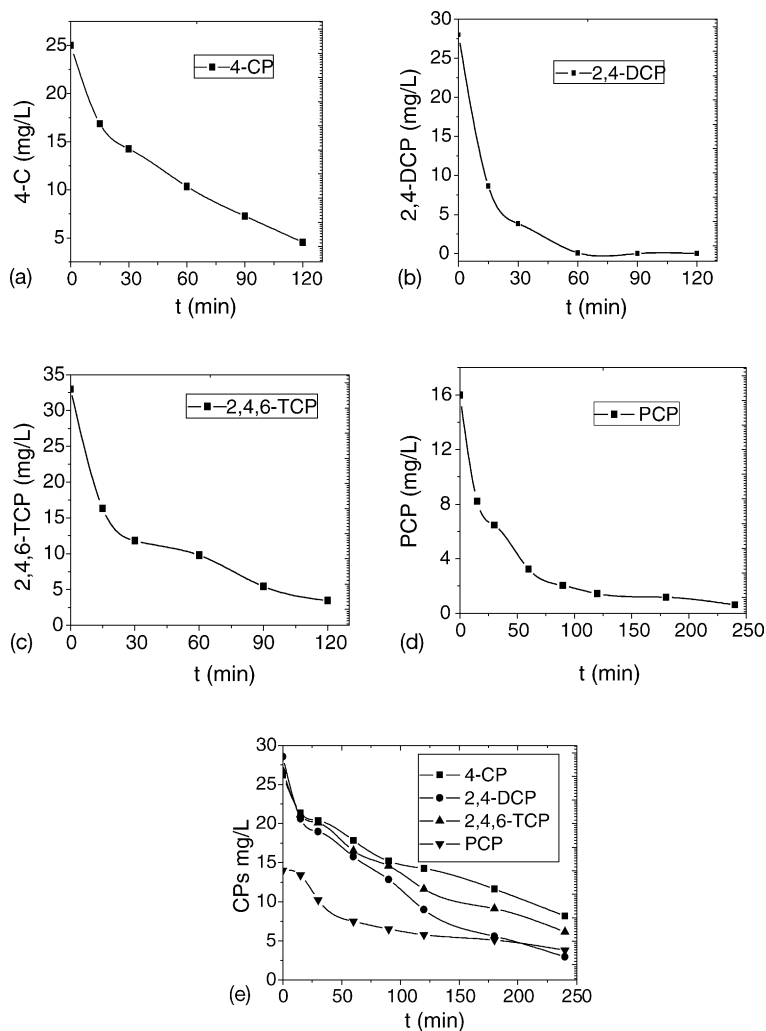

Fig. 3. Degradation of 4-CP, 2,4-DCP, 2,4,6-TCP and PCP. Conditions: 5 V voltage, 0.14 mol/L NaSO$_4$ electrolyte, pH = 2.5, 3.8 mg/L Fe^{2+}, (a) 4-CP; (b) 2,4-DCP; (c) 2,4,6-TCP; (d) PCP; (e) mixed aqueous solution of 4-CP, 2,4-DCP, 2,4,6-TCP and PCP.

Table 1
Pseudo first-order constant values determined for chlorophenols under electro-Fenton treatment

Chlorophenol	Rate constant (min^{-1})	Initial time (min)	Coefficient
4-CP	0.013	120	0.993
2,4-DCP	0.066	30	0.994
2,4,6-TCP	0.034	30	0.978
PCP	0.019	120	0.982

Table 2
Intermediates of degradation process

Chlorophenols	Intermediates
4-CP	Benzoquinone, 1,4-catechol, 4-chloro-1,2-catechol, phenol
2,4-DCP	2-Chlorophenol (2-CP), 4-CP
2,4,6-TCP	2,4-DCP, 2-CP, 4-CP
PCP	1,2-Tetrachlorocatechol, 1,4-tetrachlorocatechol, tetrachloro-p-hydroquinone, 2,3,5,6-tetrachlorophenol

of addition. The experimental results are in good agreement with other investigations [12–17].

3.3. Degradation of various chlorophenols

Under the above optimal conditions, the degradation of PCP, 4-CP, 2,4-DCP and 2,4,6-TCP are compared and shown in Fig. 3.

The kinetics of degradation was analyzed and the pseudo first-order reaction kinetics was observed at the first stage. Table 1 gives the rate constants.

Based on the above experimental results, the degradation sequence was obtained as: 2,4-DCP > 2,4,6-TCP > PCP > 4-CP. The same degradation sequence was also observed in the degradation of their mixed aqueous solution (Fig. 3(e)). It is interesting to note that our results are different from those reported in the degradation of various chlorophenols in other AOPs. The sequences were 2-CP > 2,4-DCP > 2,4,6-TCP for Fenton's reagent [18], 2,4-DCP > 2-CP > 2,3-DCP > 2,4,6-TCP for photocatalysis [20] and 2,3,4,6-TeCP > 2,4,6-TCP > 2,4-DCP > 4-CP for ozonation [5], respectively. In all these processes, hydroxyl radical or other strong electrophilic materials (like O_3) attacked aromatic ring. Chlorine is an electron-withdrawn group, so the electron density of aromatic ring and reaction ability of Cl compounds decrease with the increase of chlorine content. For the same content of chlorine in the aromatic ring, steric hindering effect would be the dominant reason of the reaction ability. While chlorine atom was less than two, a comprehensive effect of chlorine content and steric hindering appeared.

In this study, an exception of 4-CP occurred, which indicated that hydroxyl attack is not the only reason for the degradation of chlorophenols with electro-Fenton method. Other reasons may also exist. The selective dechlorination of chlorinated phenoxy herbicides in aqueous medium by electrocatalytic reduction over palladium-loaded carbon felt was investigated [29]. It was found that the dechlorination of 2,4-dichlorophenoxyacetic acid (2,4-D) occurred at 4-position very selectively. However, 2-chlorophenoxyacetic acid (2Cl-PAA) and 4-chlorophenoxyacetic acid (4Cl-PAA) were more slowly dechlorinated than 2,4-D and 2,4,6-trichlorophenoxyacetic acid (2,4,6-T). The authors gave the interpretation that the chlorine at 2-position in 2,4-D would facilitate the reductive elimination of chlorine at 4-position of 2,4-D. For 2,4-D and 2,4,6-T, the occurrence of multi-dechlorination, i.e., two chlorine atoms of 2,4-

D were removed at the stage, was strongly suggested. In this investigation, as a good reductive electrode material, graphite was used as cathode. This cathode had the similar effect of direct reductive dechlorination for chlorophenols. Therefore, it could be stated that hydroxyl attack dechlorination competed with cathode reductive dechlorination.

Some aromatic intermediates detected by GC/MS were listed in Table 2.

It could be seen from Table 2 that hydroxylation aromatic compounds were only detected in the degradation processes of 4-CP and PCP. Moreover, HPLC analysis revealed no other aromatic compounds except the initial chlorophenol added. So, in the competition of hydroxylation dechlorination and cathode reductive dechlorination, the later dominated in the degradation of 2,4-DCP and 2,4,6-TCP. The introduction of 2- and 6-position chlorine to 4-chlorophenol facilitated the cathode reductive dechlorination greatly, which contributed to the high values of the rate constants of 2, 4-DCP and 2,4,6-TCP. More steric hindering effect was observed on 2,4,6-TCP than 2,4-DCP, so the later was degraded faster. While for 4-CP, the appearance of phenol, 1,4-catechol and 4-chloro-1,2-catchol meant that both dechlorination processes happened, and it was the same for PCP. It could be concluded that a complex effect of hydroxylation dechlorination and cathode reductive dechlorination functioned in the degradation of 4-CP and PCP. The cathode dechlorination intermediates for all above chlorophenols were determined in comparison with other AOPs [4,6,7,9,10].
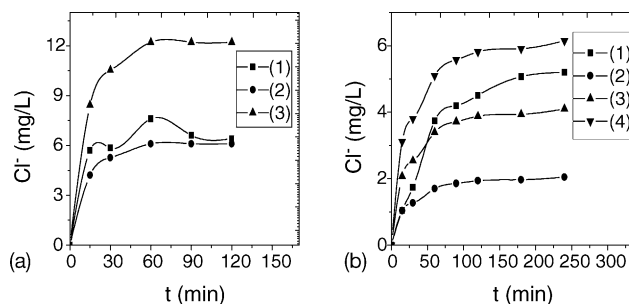

Fig. 4. A comparison of the theoretical and experimental quantities of released Cl$^-$, (a) 2,4-DCP, (1) experimental quantities of released Cl$^-$, (2) theoretical Cl$^-$ quantities with one chlorine released from 2,4-DCP, (3) theoretical Cl$^-$ quantities with two chlorine released from 2,4-DCP; (b) PCP, (1) experimental quantities of released Cl$^-$, (2) theoretical Cl$^-$ quantities with one chlorine released from PCP, (3) theoretical Cl$^-$ quantities with two chlorine released from PCP, (4) theoretical Cl$^-$ quantities with three chlorine released from PCP.
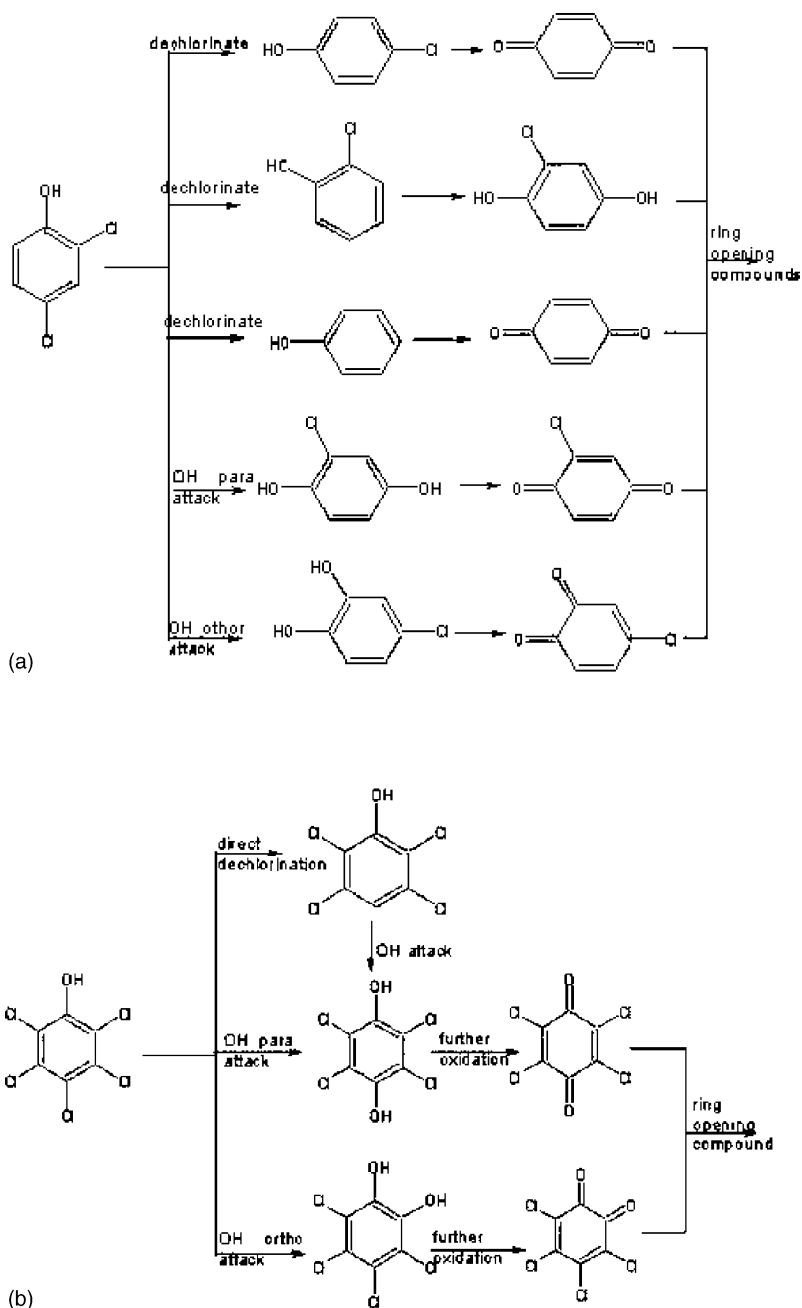
Fig. 5. Different degradation pathways. (a) PCP; (b) 2,4-DCP.

Using PCP and 2,4-DCP as representative chlorophenols, chlorine released was determined. A comparison of dechlorination between theoretical and experimental quantity released was analyzed. According to the experimental concentration changes of chlorophenols, the corresponding theoretical concentrations of Cl^- released were calculated in Fig. 4.

It could be seen that only one to two chlorines were removed for 2,4-DCP and two to three for PCP at the end of the treatment, which meant that chlorine was not released completely and some were left in the intermediates. GC/MS analysis detected Cl compounds with benzene ring, but no quantitative peaks appeared in HPLC photograph, which meant a low quantity or an unstable status of aromatic intermediates in the process. In addition, some low molecule Cl compounds such as hexachloroethane (C_2Cl_6) were detected by GC/MS. So it could be suggested that most residual chlorine was remained in the ring opening compounds.

Consequently, it could be concluded that the degradation process decreased with the increase of chlorine content with an exception of 4-CP, which might be explained by the competitive effect of hydroxyl attack dechlorination and electrochemical reductive dechlorination reaction.

3.4. Initial degradation pathways of chlorophenols

According to the above analysis, different pathways were proposed in Fig. 5 for the degradation of PCP and 2,4-DCP.

In the degradation process of 2,4-DCP (Fig. 5(a)), cathode reductive dechlorination resulted in the formation of 2-CP, 4-CP (both detected by GC/MS) and phenol. While the intermediates of 2-chloro-1,4-catechol and 4-chloro-1,2-catechol were through hydroxylation dechlorinaion. Phenol and other intermediates were very few and degraded to ring opening compounds quickly. On the other hand, for the degradation of PCP, the formation of 2,3,5,6-tetrachlorophenol was by cathode reductive dechlorination, while 3,4,5,6-catechol was formed by hydroxylation dechlorination. 2,3,5,6-Catechol was produced by hydroxylation dechlorination and the attack of hydroxyl to the free position of 2,3,5,6-tetrachlorophenol. In both processes, further oxidation generated benzoquinone derivatives. Because of the presence of direct electrochemical reductive dechlorination, some intermediates such as phenol and 2,3,5,6-tetrachlorophenol were observed in this study, different from the other AOPs [18–22].

4. Conclusions

The conclusions of this study are:

(1) The optimal conditions without Fe ion introduction were 5.0 V of cell voltage, 0.14 mol/L of Na_2SO_4 and 2.5 of pH. Under these conditions, electro-Fenton system can operate more effectively with the introduction of Fe ions.

(2) Using electro-Fenton method, the degradation sequence with various chlorophenols was obtained as 2,4-DCP > 2,4,6-TCP > PCP > 4-CP. This is different from those in other AOPs. The difference was explained as the competition of hydroxyl attack dechlorination and electrochemical reductive dechlorination.

(3) The degradation pathways of chlorophenoles were proposed as *ortho-* and *para-* reaction by hydroxyl attack and direct dechlorination by cathode reduction. The further oxidation was preceded by hydroxyl radical. Most residual chlorine was left in the ring opening low molecule compounds.

Acknowledgement

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