



## The intermediate products in the degradation of 4-chlorophenol by pulsed high voltage discharge in water

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### ABSTRACT

Degradation of 4-chlorophenol by pulsed high voltage discharge is an intricate process involving a series of complex chemical reactions. Hydroxylation of 4-chlorophenol to form hydroquinone, 4-chlororesorcinol and 4-chlorocatechol is the first step, though a very small amount of direct cleavage products of the C<sub>1</sub>–C<sub>2</sub> or C<sub>5</sub>–C<sub>6</sub> bond are observed. The yield of 4-chlorocatechol is about twice as much as that of hydroquinone. Less 4-chlororesorcinol is produced. The free chloride ions dropped from the 4-chlorophenol degradation can obtain reactivity again from the discharge, and react with undegraded 4-chlorophenol to form 2,4-dichlorophenol. Some ring-opened products have also been identified and their possible reaction routes are proposed. Several compounds are verified by use of authentic samples. The more stable ring-opened products are low molecular weight (LMW) acids such as formic, acetic, oxalic, malonate, maleic and malic acid. By discharging 4-chlorophenol aqueous solution for 36 min, the amount of carbons obtained from organic acids is more than 50% while that of carbons from aromatic products less than 20% in the carbons of degraded 4-chlorophenol, which is about 94% of initial carbons. After 60 min of discharge, all the 4-chlorophenol and its aromatic intermediates have been removed completely and the organic carbons are mainly presented as organic acid such as acetic and oxalate acid. At the end of the 120 min discharge, the amount of the remaining organic carbons is not more than 14% of the initial carbons.

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### 1. Introduction

As one of the advanced oxidation technologies, pulsed high-voltage discharge has generated a lot of interest in applications including organic contaminants removal [1–3]. The technology has been used in wastewater treatment for some years, because it could induce an oxidation process leading to the degradation of organic contaminants [4–7].

Aromatic organics have been the most extensively investigated contaminants in the degradation process [8–10]. Among these contaminants, 4-chlorophenol has been often chosen to evaluate the experimental parameters [11–13]. The 4-chlorophenol degradation by pulsed high voltage discharge is an intricate process involving a series of complex chemical reactions. Willberg and Lang suggested that the degradation of organic contaminants was primarily due to photochemical processes. However, oxidation within the plasma channel was a significant secondary oxidative process at high substrate concentrations [14]. Hoeben et al. found that corona discharges with Ar bubbling caused mainly hydroxylation of the organic contaminant presented in the aqueous solution

[15]. If oxygen was present, the organic contaminant was degraded by bond/ring cleavage due to oxygen/ozone attack on the radical hydroxylated derivatives of the organic contaminant. Zhang et al. got the same conclusion when oxygen gas was bubbled into the aqueous solution of organic contaminants [16]. In the case of nitrogen bubbling, they claimed that hydroxylation of organic contaminant was the main pathway of degradation with the attack of N atom on organic contaminant.

As far as 4-chlorophenol degradation process was concerned, the intermediates in the earliest stages, a number of aromatic compounds, have been reported. Tezuka and Iwasaki proposed that the successive attack of hydroxyl radicals on the benzene ring was presumed to be the key steps in the degradation reaction pathway [17]. Du et al. stated that the main intermediates of 4-chlorophenol degradation were *p*-benzoquinone, hydroquinone, 4-chlorocatechol, *p*-chloronitrobenzene and ring cleavage products (acetic acid, glycol, propanone, and others) [12]. Wang confirmed the formation of phenol, hydroquinone and 4-chlorocatechol during 4-chlorophenol degradation [13]. Lukes et al. concluded that the electrophonic attacks by hydroxyl radicals and ozone were the main oxidation pathways for the degradation of phenols under argon and oxygen atmospheres [18]. Although the initial steps of 4-chlorophenol degradation are known, little is known about the chemical degradation steps beyond the first two.

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In the present study, various in-process products are identified to illustrate the pathways of 4-chlorophenol degradation in the pulsed high voltage discharge system. In the discharge system, bubbling gas was often employed to improve the discharge characteristic in the non-equilibrium field [19–21]. Air was used for the sake of convenience. There is about 79% of nitrogen and 21% of oxygen in air. It was confirmed that the types and the density of the main radicals induced by discharge was different with bubbling different gases [22–24]. Consequently, the degradation mechanisms of phenol or substituted phenols under Ar, O<sub>2</sub>, N<sub>2</sub>, or air in pulsed high voltage discharge system were different [15,16,18]. Correspondingly, the degradation intermediates of 4-chlorophenol should be different with bubbling different gases. The objective of this study is to determine the degradation intermediates of 4-chlorophenol by pulsed high voltage discharge with bubbling oxygen, with particular focus on the important ring-opening steps. The GC-MS, HPLC and Ion Chromatograph analyses have been used for detections of the degradation intermediates. The main aromatic compounds are not only identified but also quantified, and the carbon balance during 4-chlorophenol degradation is conducted. In addition, some minor products are identified, which offers the clues for some bond/ring cleavage reactions. The formation mechanism of some compounds is discussed. Eventually, the potential pathway of 4-chlorophenol degradation is suggested.

## 2. Experimental

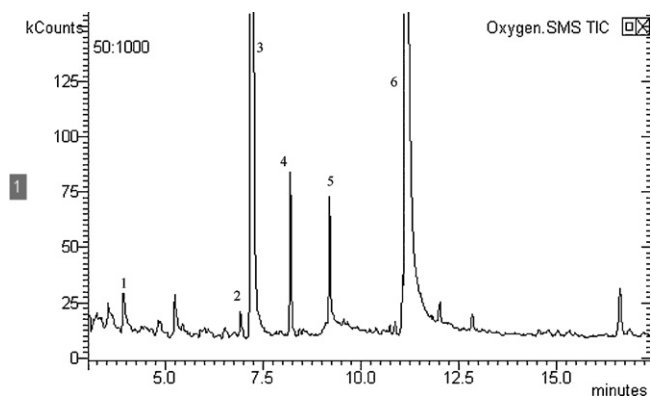
### 2.1. The discharge system

The pulsed high voltage power supply and the reactor were the same as that in our former work [25]. In all experiments, the applied voltage was 25 kV with 140 Hz. The original 300 mL 4-chlorophenol solution with the concentration of 100 mg L<sup>-1</sup> was poured into the reactor through the upper end of the reactor. The discharge experiments were carried out after the gas flux was stabilized at 120 L h<sup>-1</sup> and the voltage was adjusted to 25 kV. (The time for rising voltage from 0 to 25 kV was about 20 s.) After certain time, the discharged solution was taken out of the reactor for analyses. All discharge experiments were conducted more than three times and the reproducibility was within 8%.

### 2.2. Analysis methods

#### 2.2.1. GC-MS analyses

The GC-MS detection was used for qualitative analysis of intermediate products resulted from the 4-chlorophenol degradation by pulsed high voltage discharge. In preparing the discharged solution for GC-MS detection, 300 mL 4-chlorophenol solution with the concentration of 100 mg L<sup>-1</sup> was discharged for certain time and then separated in triplicate. Two of them were moved into two 200 mL extracting bottles (glass, medical bottle). Immediately, 30 mL ethyl acetate was added into one bottle (Sample A) and 30 mL diethyl ether into the other one (Sample B). The bottles were sealed with plugs and then shaken in a horizontal direction at 200 times per minute for 30 min. The temperature was kept at 15 °C. After 30 min extraction, the mixed liquid was moved into a separating funnel. After the organic phase was separated from the water phase, 10 mL sample was taken from each extraction layer and transferred into two sample bottles. The injected samples were 5 μL. In preparing sample C, 5 mL solution was taken out of the remaining 100 mL discharged solution mixed with 5 mL formic acid and transferred into a sample bottle. The injected sample was 1 μL. It should be mentioned that each discharge experiment for preparing the GC-MS detection samples was performed with the original 4-chlorophenol



**Fig. 1.** The total ion current (TIC) chromatogram of sample A after discharging the 4-chlorophenol solution for 24 min.

solution of 300 mL (i.e., the discharge was stopped when the original 4-chlorophenol solution was treated by discharge for assured time and another experiment was performed again with a new solution).

The temperature programs of column oven for three samples are shown in Table 1.

#### 2.2.2. HPLC analysis

The concentration of aromatic products such as 4-chlorophenol, *p*-benzoquinone (peak 1), hydroquinone, 2,4-dichlorophenol, 4-chlororesorcinol and 4-chlorocatechol were all determined by a Waters 1525 HPLC equipped with a 2489 UV/visible detector and μBondapak™ C<sub>18</sub> column (PN27324, 3.9 mm × 300 mm). The *p*-benzoquinone was detected at 250 nm and the other substances were routinely determined at 280 nm. The eluent was 0.5 mmol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution with a flow rate of 0.8 mL min<sup>-1</sup> and methanol with a flow rate of 0.2 mL min<sup>-1</sup>. The identification of the intermediates by HPLC was performed by the comparison of the retention time of the peak in the discharged sample with that in the authentic sample. The concentrations of compounds were calculated by using the equations derived from the calibration measurements for authentic substances. The error for HPLC analyses was not more than 1%.

#### 2.2.3. Ion Chromatograph analysis

The organic acids and free chloride ions were determined by a Metrohm 861 Advanced Compact Ion Chromatograph equipped with an ASSUP 5 column (4.0 mm × 250 mm). The mobile phase was composed of sodium carbonate (3.2 mmol L<sup>-1</sup>) and sodium bicarbonate (1.0 mmol L<sup>-1</sup>) solutions with a flow rate of 0.6 mL min<sup>-1</sup>. The identification and concentration calculation was similar to the method used in HPLC analysis. The error for Ion Chromatograph analysis was not more than 1%.

## 3. Results and discussions

### 3.1. The aromatic intermediates of 4-chlorophenol degradation

The gas chromatograph–mass spectrometer (GC–MS) is often used to identify unknown substances. In present study, the intermediates of 4-chlorophenol degradation in a pulsed high voltage discharge system were traced by using four different instruments. On the whole, the degradation intermediates of 4-chlorophenol could be divided into two groups: aromatic compounds and ring-opened products. Some inferences about the microscopic chemical processes may be drawn from these products.

The aromatic products identified by GC-MS were similar in the different samples prepared. e. The results of sample (A) are shown in Figs. 1 and 2. It is seen that the typical aromatic intermedi-

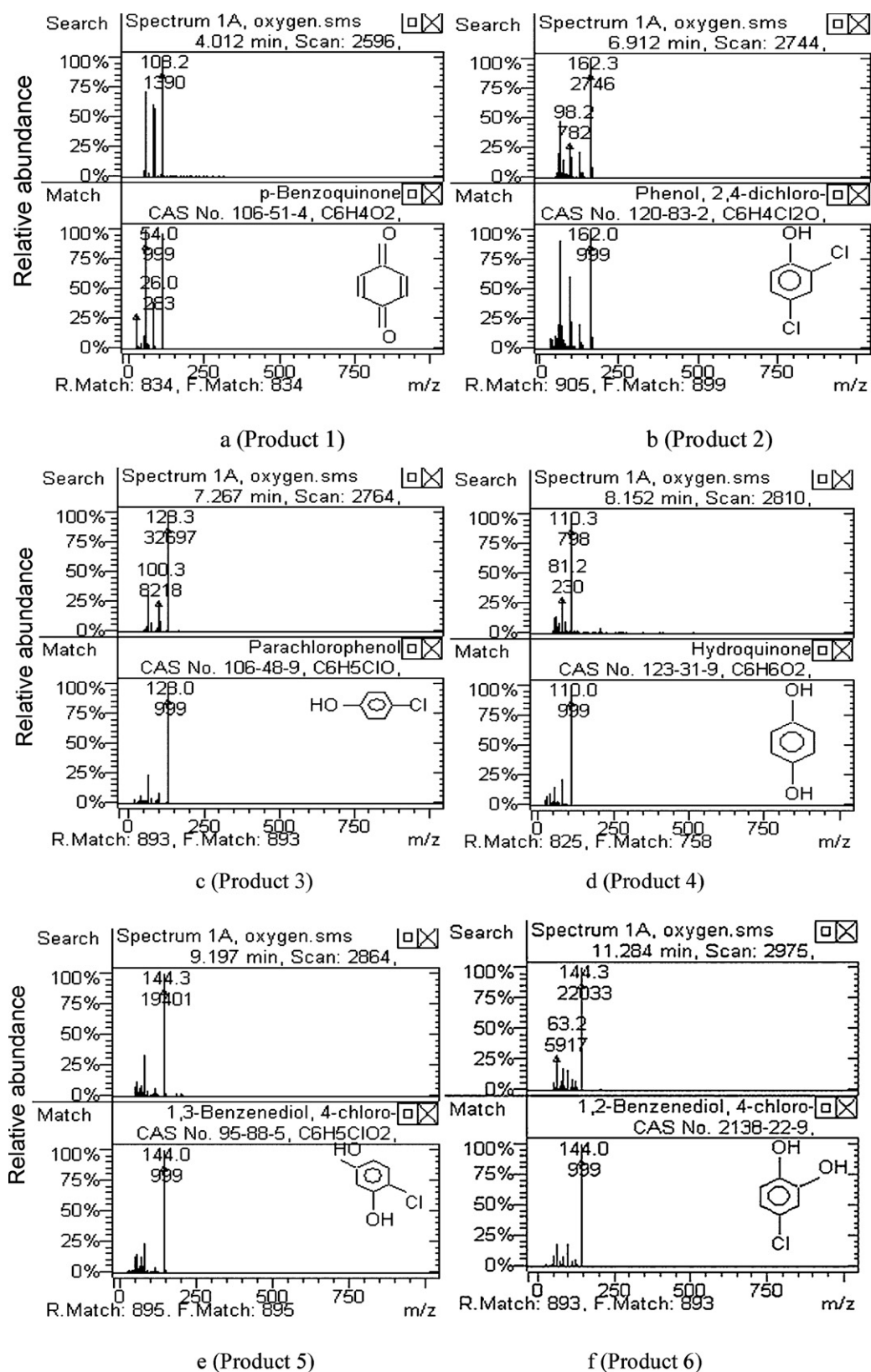


Fig. 2. The MS chromatogram of the six aromatic compounds.

ates during 4-chlorophenol degradation are *p*-benzoquinone (peak 1, Fig. 2(a)), 2,4-dichlorophenol (peak 2, Fig. 2(b)), hydroquinone (peak 4, Fig. 2(d)), 4-chlororesorcinol (peak 5, Fig. 2(e)) and 4-chlorocatechol (peak 6, Fig. 2(f)).

It has been confirmed that the active species such as H<sub>2</sub>O<sub>2</sub>, •OH and O<sub>3</sub> could be generated in a pulsed high voltage discharge system [22–24]. The •OH is the most reactive one [17]. It could attack the para- or ortho-position of the OH group to

**Table 1**

The temperature programs of column oven for the three samples.

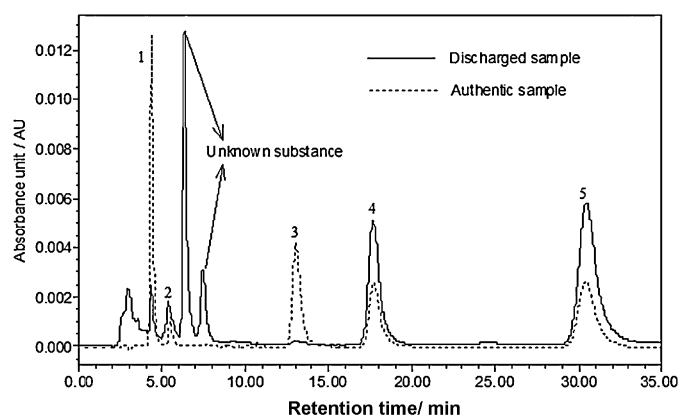
	A				B			C				
Temperature (°C)	80.0	135.0	150.0	250.0	35.0	50.0	110.0	150.0	250.0	50.0	100.0	230.0
Rate (°C/min)	0.00	20.00	5.00	20.00	0.0	5.00	10.00	5.00	20.00	0.00	10.00	20.00
Hold (min)	3.00	1.00	15.00	20.00	3.00	0.00	0.00	10.00	10.00	3.50	1.00	20.00
Total (min)	3.00	6.75	24.75	49.75	3.00	6.00	12.00	30.00	45.00	3.50	9.50	36.00

form 4-chlorocatechol (the product 6) or 4-chlororesorcinol, or substitute the Cl group of 4-chlorophenol to produce hydroquinone (the product 4). The detection of product 4, product 5 and product 6 confirmed these reactions. From Fig. 1, it is seen that the peak area of the 4-chlorocatechol is much larger than that of the 4-chlororesorcinol and hydroquinone, suggesting the yield of 4-chlorocatechol is much higher than other intermediates.

The formation of four aromatic products was also verified by the HPLC detection. Fig. 3 shows the HPLC spectra of the authentic and discharged samples. It could be seen that the peak of hydroquinone (peak 1), *p*-benzoquinone (peak 2), 4-chlororesorcinol (peak 3), 4-chlorocatechol (peak 4) or 4-chlorophenol (peak 5) in the discharged sample matches well respectively with that in the authentic sample.

The radical chain reaction was induced by discharge and several free chloride ions dropped from 4-chlorophenol degradation could get reactivity from the discharge system. The active free chloride ions could react with the undegraded 4-chlorophenol to produce 2,4-dichlorophenol (product 2). But the 2,4-dichlorophenol was only detected by GC-MS. In the HPLC measurement, 2,4-dichlorophenol was not found, suggesting its extremely low yield in the discharge system.

Further experiments were carried out for the quantitative analysis of hydroquinone, *p*-benzoquinone, 4-chlorocatechol and 4-chlororesorcinol. Fig. 4 shows the results. It is seen that the concentrations of these four products increased in the first 30 min and then decreased. At the same discharge time, the concentration of 4-chlorocatechol is much more than that of others, which is in agreement with the results from the GC-MS detection. *p*-Benzoquinone could be detected as the further degradation of hydroquinone, because hydroquinone is easy to lose two H and generate *p*-benzoquinone. It may be speculated that *p*-benzoquinone in the discharge system was all transformed from hydroquinone.



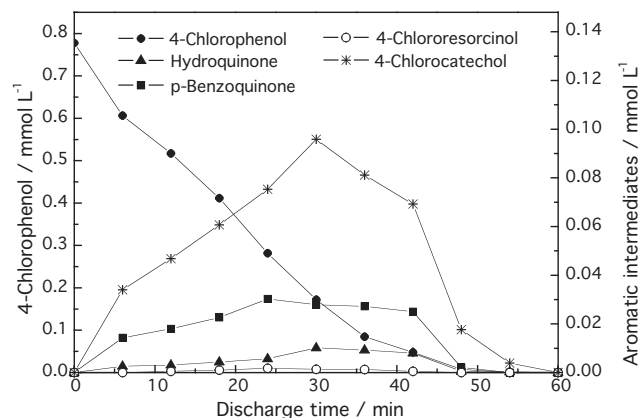
**Fig. 3.** The HPLC spectra of the authentic and discharged samples at 280 nm. Note: the peak numbered in sequence is hydroquinone (peak 1), *p*-benzoquinone (peak 2), 4-chlororesorcinol (peak 3), 4-chlorocatechol (peak 4) and 4-chlorophenol (peak 5), respectively; the concentrations of the standard substances in the authentic sample were all set at 7 mg L<sup>-1</sup>; the initial 4-chlorophenol solution of 100 mg L<sup>-1</sup> was discharged for 30 min; Calibrated with authentic samples, the concentration of these five compounds in the sample is 1.13, 3.00, 0.19, 13.80 and 24.15 mg L<sup>-1</sup>, respectively, in peak No. sequence.

The true yield of hydroquinone derived from 4-chlorophenol should be the sum of the hydroquinone and *p*-benzoquinone. At the 6th min and 12th min, the total yield of hydroquinone and *p*-benzoquinone was about 0.016 mmol L<sup>-1</sup> and 0.021 mmol L<sup>-1</sup>, respectively, while the concentration of 4-chlorocatechol was 0.034 mmol L<sup>-1</sup> and 0.048 mmol L<sup>-1</sup>, respectively. These intermediates could be degraded as well in the discharge system, but the majority of the active species might be trapped by 4-chlorophenol due to its much higher concentration in the early stage of discharge. The yields before 12 min are more close to the real productivity of these intermediates. Therefore, the productivity of 4-chlorocatechol and hydroquinone originally resulted from 4-chlorophenol is about 2:1 in the 4-chlorophenol degradation process by discharge. In a 4-chlorophenol molecule, there are two ortho-positions of the OH group, but only one Cl group. Therefore, the chance of forming 4-chlorocatechol by \*OH attack is about twice as much as that of hydroquinone. Moreover, both the OH and Cl groups are ortho-para directing groups, but the activity of the OH group is higher than that of the Cl group. The ortho-position of the OH group is easier to be attacked, and the yield of 4-chlorocatechol (product 6) is much higher than that of 4-chlororesorcinol (product 5).

### 3.2. The ring-opened products of 4-chlorophenol degradation

Combining GC-MS with Ion Chromatograph detection, 18 kinds of ring-opened products from 4-chlorophenol degradation were determined (Table 2).

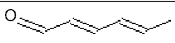
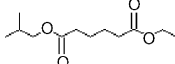
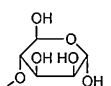
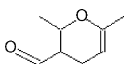
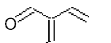

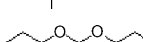
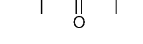
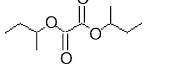

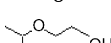


The product 7 ((*E,E*)-2,4-hexadienal) was identified in all the formic acid diluting samples (C) with the discharge time of 6, 12, 18, 24, 30 and 36 min. The product 8 was determined in the diethyl ether extracted samples (B) with discharge time of 24 min and 30 min. The product 9 was only detected at the first 6 min. The product 10 was identified in the prepared sample series of B and C at 6, 12, 18, 24 and 30 min. The peaks of these compounds were all very low, suggesting their low yields in the discharge reactor. However, these products presented the important clues for tracing the ring-opening reaction in the degradation process



**Fig. 4.** The concentration of 4-chlorophenol and its aromatic intermediates during discharge.

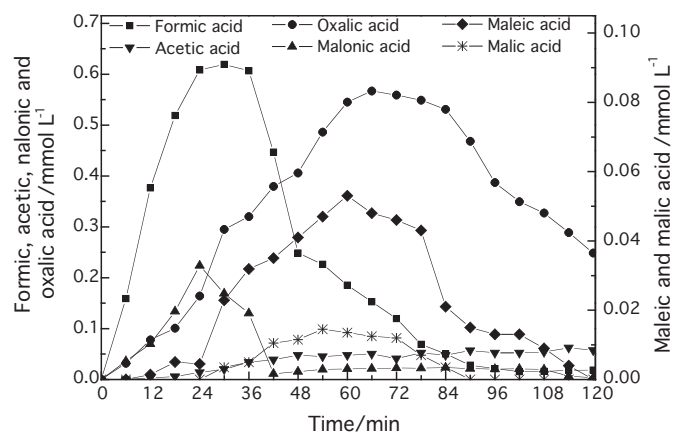


**Table 2**  
The ring-opened products resulting from 4-chlorophenol degradation, detected by GC-MS.

Product No.	Product structure	Sample Preparation methods	Discharged time (min)	Retention time (min)
7		C	6–36	6.709
8		B	24, 30	15.371
9		C	6	8.185
10		B,C	6–18	13.163 (B) 11.794 (C)
11		C	6–36	7.879
12		C	36	6.019
13		C	6–36	9.253
14		C	12–36	7.875
15		B	30	14.613
16		C	18–24	4.322
17		B	30	4.775
18		B	30	7.501
19		B, C	30	3.317(B) 6.845 (C)

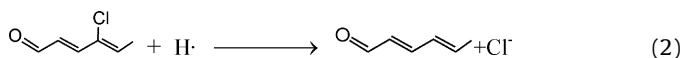
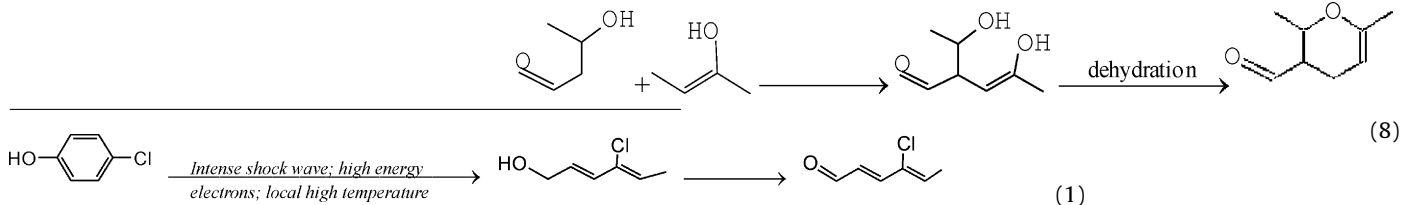
of 4-chlorophenol. In addition, some alkanes were detected in all the prepared samples for GC-MS measurement, especially in the formic acid diluted and diethyl ether extracted samples, suggesting the formations of methyl and alkyl free radicals in the discharged samples. Six organic acids such as formic, acetic, oxalic, maleic, malonic and malic acid were detected by a Metrohm 861 Advanced Compact Ion Chromatograph. The peak of each substance in the discharged sample matched well with that in the authentic sample, suggesting the generation of these six LMW organic acids [25]. It was thought that the main ring-opened products were LMW organic acids such as formic (product 20), acetic (product 21), oxalic (product 22), malonic (product 23), maleic (product 24) and malic acid (product 25). Fig. 5 shows the concentration of the organic acids during 4-chlorophenol degradation in 120 min. It is seen that the formic, oxalic and malonic acids were detected from the first 6 min, the acetic and maleic acids were detected from 12 min with a concentration of not more than  $0.05 \text{ mmol L}^{-1}$  and the malic acid was detected from 30 min with a concentration of not more than  $0.02 \text{ mmol L}^{-1}$ . Except acetic acid, the concentrations of other acids increased to a maximum value and then decreased after the turning point. From 6 to 42 min, the predominant acid formed was formic acid, while after 48 min oxalic acid was the predominant one. At the end of 120 min discharge, the concentration of oxalic acid was about  $0.25 \text{ mmol L}^{-1}$ , while the overall concentration of other five organic acids was not more than a third of that of the oxalic acid.

In fact, not all intermediates can be verified using the available methods presented in this work. Some active intermediates could not be identified. Nevertheless, we could still infer the formation path of one detected product from its molecular structure, other intermediates and the original substance.



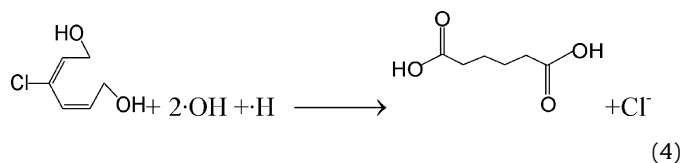
**Fig. 5.** The concentrations of organic acids resulted from 4-chlorophenol degradation by discharge.

The product 7, 8 or 9 each contains a 6-carbon structure. In the pulsed high voltage discharge system, not only the chemical processes such as the formations of active species but also the physical processes such as strong *uv* light, local high temperature and intense shock waves were stimulated [26–29]. As large amount of formic acid was added into the discharged sample, more  $H^{\bullet}$  could be activated to form  $H^{\bullet}$  radical. The product 7 (2,4-hexadienal) may be produced by the following reactions:



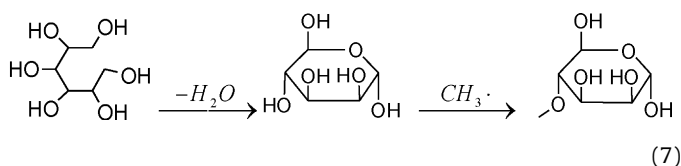
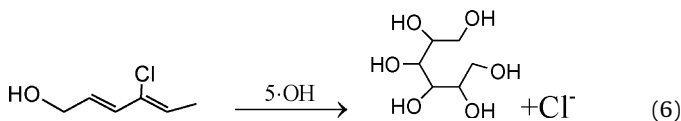
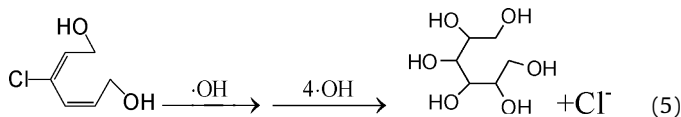
Therefore, the detection of product 7 indicates that the 4-chlorophenol ring could be directly opened by the physical processes, resulting from the cleavage of the  $C_1$ – $C_2$  or  $C_5$ – $C_6$  bond.

The main precursor of product 8 was hexanedioic acid which could be formed in the following way:

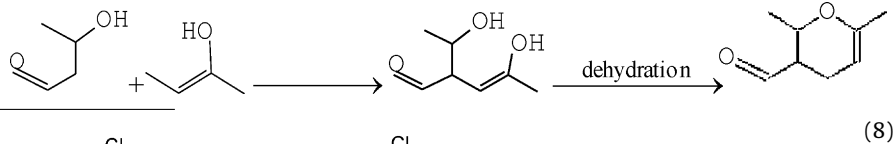


Hexanedioic acid was further reacted with 2-methyl-propanol, and the product 9 was generated after the intermolecular dehydration.

The product 9 was only detected at the first 6 min as 4-chlorophenol was the main reactant in the discharge system. It was thought that the  $\cdot\text{OH}$  attack was the main force for the degradation of organic contaminants in the discharge system [17]. From the formation of product 7, it is clear that the  $C_1$ – $C_2$  or  $C_5$ – $C_6$  bond in the 4-chlorophenol could be directly broken during the discharge. The product resulted from the cleavage of  $C_1$ – $C_2$  or  $C_5$ – $C_6$  bond is easy to react with  $\cdot\text{OH}$  to generate hexanehexol. The product 9 could be formed by intermolecular dehydration of hexanehexol with an additive reaction induced by  $\text{CH}_3^{\bullet}$ :

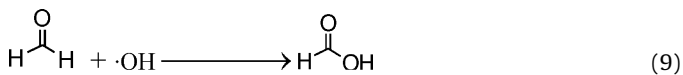


The product 10 was also found in the degradation process of hydroquinone, *p*-benzoquinone and 4-chlorocatechol, suggesting it might be the outcome of their further degradation. The formation mechanism of the product 10 was complex. If the pulsed high voltage power is turned off and the initiation of active radicals is stopped, the termination reactions between different radicals will be intensified. The product 10 may be the resultant of the reaction between 3-hydroxybutyaldehyde and crotonyl alcohol:

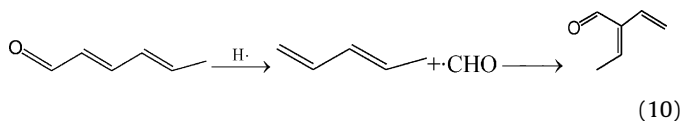


The detection of product 10 implies the formation of 3-hydroxybutyaldehyde and crotonyl alcohol. In fact, similar structure as crotonyl alcohol could be found in other detected compounds. We could conjecture the formation path from the discharge mechanism coupling with the theory of organic chemistry, as shown in Fig. 6.

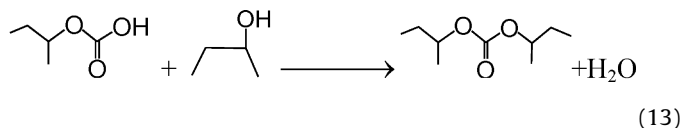
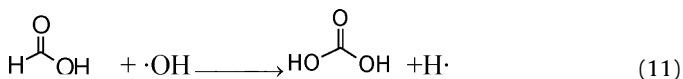
It was confirmed that organic acids such as formic, acetic, oxalic, malonate and maleic acid were formed during 4-chlorophenol degradation in the pulsed high voltage discharge system. Formic acid was the oxydate of formaldehyde:



The product 11 may be the further degradation product of the product 8:



The products 12, 13, 14 and 15 contain the structure of tert-butyl alcohol. It was confirmed that the formic acid was produced during the 4-chlorophenol degradation process, and large amount of formic acid was added in the process of preparing sample C. The formic acid could take part in the radical reaction and then the product 13 may be formed by the following reactions:



It was also confirmed that the oxalic acid was formed during the 4-chlorophenol degradation by the pulsed high voltage discharge. Consequently, the product 14 could be generated in the similar way by the reaction of tert-butyl alcohol with oxalic acid.



**Table 3**The carbon percentages ( $P_t$ , %) of main intermediate product in the initial carbons.

Product No.	1	4	5	6	20	21	22	23	24	25
6 min	1.83	0.33	0.00	4.37	3.41	0.00	1.37	2.31	0.00	0.00
12 min	2.31	0.40	0.07	6.01	8.07	0.13	3.34	4.50	0.12	0.00
18 min	2.91	0.56	0.12	7.81	11.12	0.25	4.33	8.62	0.43	0.00
24 min	3.89	0.72	0.22	9.68	13.04	0.60	7.03	14.40	0.39	0.00
30 min	3.58	1.30	0.17	12.32	13.27	0.86	12.65	10.87	1.96	0.30
36 min	3.50	1.19	0.16	10.43	13.00	1.46	13.72	8.36	2.73	0.43
42 min	3.22	1.03	0.06	8.90	9.58	1.67	16.27	0.74	3.00	0.90
48 min	0.27	0.07	0.00	2.26	5.33	2.04	17.40	1.00	3.52	0.99
54 min	0.00	0.03	0.00	0.50	4.85	1.93	20.83	1.25	4.03	1.24
60 min	0.00	0.00	0.00	0.00	3.98	2.04	23.36	1.35	4.54	1.16
66 min	–	–	–	–	3.27	2.14	24.31	1.38	4.12	1.07
72 min	–	–	–	–	2.56	1.76	23.96	1.45	3.94	1.03
78 min	–	–	–	–	1.48	2.25	23.53	1.41	3.69	0.60
84 min	–	–	–	–	1.07	2.04	22.76	1.51	1.80	0.30
90 min	–	–	–	–	0.60	2.44	20.06	1.38	1.29	0.00
96 min	–	–	–	–	0.46	2.25	16.59	1.32	1.11	0.00
102 min	–	–	–	–	0.33	2.25	14.98	1.35	1.11	0.00
108 min	–	–	–	–	0.34	2.31	14.02	1.25	0.77	0.00
114 min	–	–	–	–	0.39	2.68	12.37	0.42	0.34	0.00
120 min	–	–	–	–	0.40	2.46	10.65	0.23	0.00	0.00

Note: The product 1, 4, 5 and 6 is *p*-benzoquinone, hydroquinone, 4-chlororesorcinol and 4-chlorocatechol, respectively. The products 20–25 are formic, acetic, oxalic, malonate, maleic and malic acid in sequence.

maleic acid but it is 2 for acetic acid;  $W_t$  is the carbon content of certain substance, which is the concentration of the substance multiplied by the carbon numbers in its molecule. For example, the total aromatic carbons (total Aro. Carbons) is calculated as the sum of  $C_t$  of every aromatic substance in the discharged solution (intermediate products 1, 4, 5 and 6 and the  $C_{t-4CP}$ ) multiplied by 6 while the carbon content of aromatic products is calculated as the overall concentration of aromatic intermediates (products 1, 4, 5 and 6) multiplied by 6;  $P_t$  (%) is the mass percentage of carbons of certain intermediate product to the carbons in the original 4-chlorophenol solution ( $C_{0-4CP} \times 6 \text{ mmol L}^{-1}$ ); On the contrast,  $R_t$  is the mass percentage of carbons of certain intermediate product to the carbons of the degraded 4-chlorophenol at  $t$  time.

The results of  $P_t$  are shown in Table 3. From Table 3, it is seen that the 4-chlorophenol is converted into aromatic products as well as organic acids from the first 6 min. About 4.37% of original carbons were converted into 4-chlorocatechol (product 6) while 3.4% into formic acid (product 20) as the degraded 4-chlorophenol was about 22% at 6 min. But after 60 min, the concentrations of all the aromatic substances are lower than the detection limits and the main constituents from 4-chlorophenol degradation are organic acids. The dominant aromatic product is 4-chlorocatechol from 6 to 54 min while the dominant organic acid is different at different discharge stages. The  $P_t$  of formic acid is much higher than that of other organic acids before 18 min, while it changes little from 24 to 36 min and decreases from 36 to 90 min. After 90 min, it changes little and is about 0.40% at 120 min. During 120 min discharge, the  $P_t$  of acetic acid increases slightly before 42 min and then changes a little. At the end of 120 min, it is about 2.46%, which is only next to the carbon percentage of oxalic acid. The  $P_t$  of oxalic acid increases before 54 min and then decreases slowly. At the end of 120 min discharge, it is about 10.65% and is the highest in the discharged 4-chlorophenol solution. The  $P_t$  of malonate increases almost lineally before 24 min and is slightly higher than that of the formic acid at 24 min but lower at 30 min and 36 min. After 42 min, it has only a slight variation. The carbon percentages of maleic acid increases from 12 min and reaches its maximum value at 60 min. From 60 to 114 min, it decreases to about 0.34%.

Fig. 7(a) shows the carbon distribution during 4-chlorophenol degradation from 0 to 120 min. The carbon content of the removed 4-chlorophenol (Removed 4-CP) increases with the discharge time

while that of the Undegraded 4-chlorophenol (Undegraded 4-CP) decreases from 0 to 48 min. After 54 min, the carbon content of the removed 4-CP is close to that of the initial 4-chlorophenol and the carbon content of the Undegraded 4-CP decreases to zero because all the initial 4-chlorophenol have been transformed to other compounds in 54 min of discharge (Fig. 4). The carbon content of aromatic products increases and reaches a maximum value at 30 min and then decreases. The total carbon content of aromatic substances, including undegraded 4-chlorophenol and its aromatic intermediates, decreases with the discharge time from 0 to 54 min. From 60 min, there are almost no aromatic carbons determined. The carbon content of organic acids reaches its maximum value at 36 min and then decreases from 42 to 120 min. At the end of the 120 min of discharge, there were about  $0.66 \text{ mmol L}^{-1}$  carbon of organic acids remained in the discharged solution.

Fig. 7(b) shows the carbon percentage of different substances in the removed 4-chlorophenol ( $R_t$ ). It is seen that the organic acid accounts for the most of the carbons in the removed 4-chlorophenol during all the discharge time. The carbons of organic acid take up more than 50% while the carbons of aromatic products less than 30% in the total carbons of removed 4-chlorophenol ( $C_{RL-4CP}$ ) from 12 min. The sum of the quantified aromatic products and organic acid occupies more than 70% of the carbons in the removed 4-chlorophenol by 36 min discharge, suggesting that the most of the removed 4-chlorophenol still remains organic structure in the discharged solution. From 42 min, the carbon percentages of aromatic intermediates decrease sharply and achieves to almost zero at 60 min. After 60 min, all the aromatic products and 4-chlorophenol has been degraded completely and the organic carbons is mainly presented as organic acid. At the end of the 120 discharge, the remaining organic carbons were not more than 14% of the initial carbons.

### 3.4. The degradation pathway of 4-chlorophenol

With the identification of intermediate products, the degradation pathways of 4-chlorophenol could be traceable. From the first degradation step, the hydroquinone, 4-chlororesorcinol and 4-chlorocatechol are derived from the hydroxylation reactions. Less 4-chlororesorcinol is produced. Several free chloride ions dropped from the 4-chlorophenol could get reactivity from the discharge



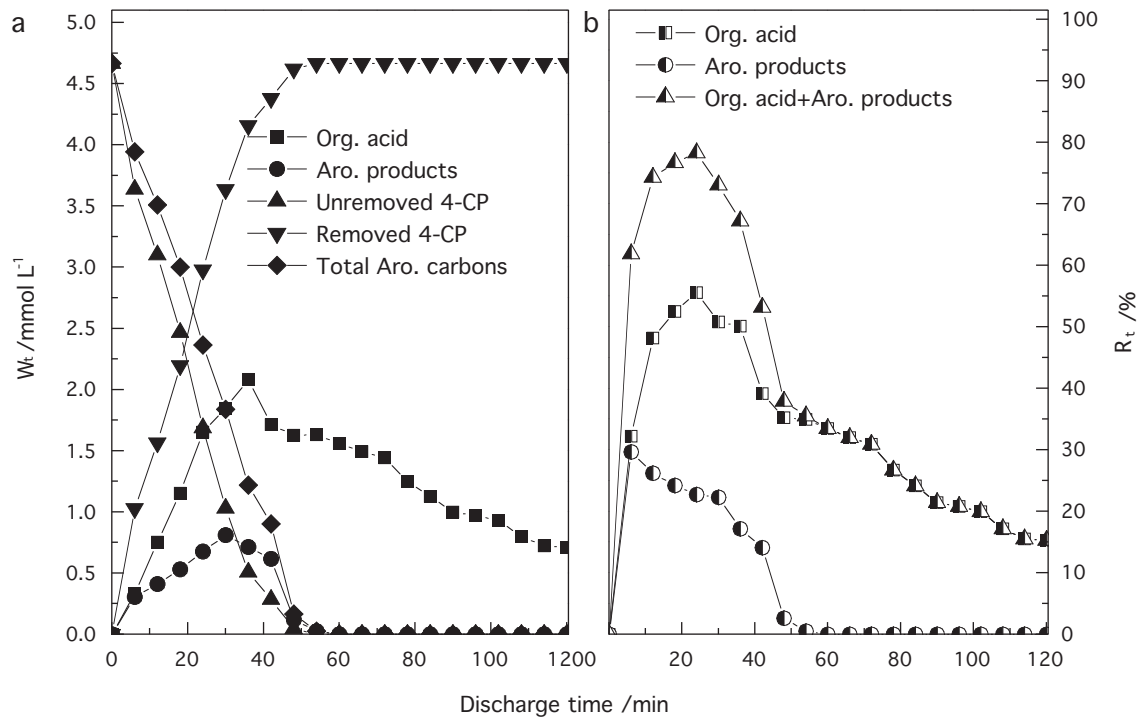


Fig. 7. The carbon balance during 4-chlorophenol degradation.

system, by reacting with undegraded 4-chlorophenol to produce small amount of 2,4-dichlorophenol. Most of the ring-opened products detected by GC-MS contain the fragment derived from the bond breakage of 4-chlorophenol, but the more stable ring-opened

products are LMW organic acids such as formic, acetic, oxalic, malonate, maleic and malic acid. The ring of the 4-chlorophenol could be directly opened by breaking the  $C_1-C_2$  or  $C_5-C_6$  bond, forming 4-chloro-2,4-hexadien-1-ol. If following the path of hydroquinone

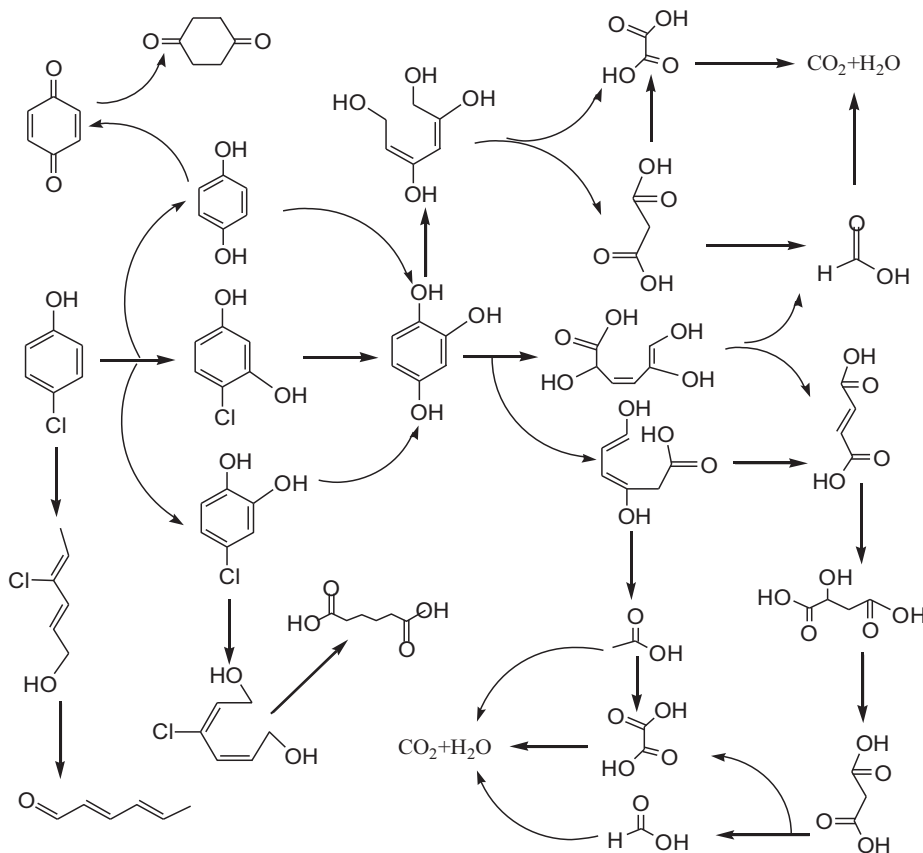


Fig. 8. The representative pathways of 4-chlorophenol degradation by pulsed high voltage discharge.

or 4-chlorocatechol formation, the four-carbon structure such as 3-hydroxybutyraldehyde is formed subsequently. Combining all the analytic results together, some pathways of 4-chlorophenol degradation could be suggested, as shown in Fig. 8.

#### 4. Conclusion

4-Chlorophenol degradation by pulsed high voltage discharge is chiefly induced by the attack from OH, mainly producing 4-chlorocatechol, hydroquinone, and 4-chlororesorcinol in its first degradation step. The production of 4-chlorocatechol is about twice as that of hydroquinone. Less 4-chlororesorcinol is produced, because the ortho-position of the OH group is more active than that of the Cl group in a 4-chlorophenol molecule. Several free chloride ions dropped from 4-chlorophenol degradation could be reactivated in the discharge system and react with 4-chlorophenol to produce small amount of 2,4-dichlorophenol.

The ring-opening reaction could be caused by the direct breakage of the C<sub>1</sub>–C<sub>2</sub> or C<sub>5</sub>–C<sub>6</sub> bond of the 4-chlorophenol, producing 4-chloro-2,4-hexadien-1-ol. This bond breakage might be resulted from other confirmed process such as high energy electrons, intense shock wave or local high temperature. The four-carbon structure molecules such as 3-hydroxybutyraldehyde and tert-butyl alcohol are formed. The more stable ring-opened products are LMW organic acids such as formic, acetic, oxalic, malonate, maleic acid and malic acid, which are the oxidation products of the corresponding alcohol or ketone.

The 4-chlorophenol is converted into aromatic products as well as organic acids from the first 6 min of discharge. The dominant aromatic product is 4-chlorocatechol, while the dominant organic acid is different at different stages of the discharge. The carbon distribution of aromatic products and organic acids in the removed 4-chlorophenol is as follows: the carbons of organic acid take up more than 50% while the carbons of aromatic products not more than 20%; the sum of the quantified aromatic products and organic acids account for about 70% of the total carbons in the removed 4-chlorophenol by 36 min discharge. After 60 min, the aromatic products has been degraded completely and the remaining organic carbons is about 14%, which is mainly presented as acetic and oxalate acids.

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#### References

- [1] M. Magureanu, D. Piroi, N.B. Mandache, V. David, A. Medvedovici, V.I. Parvulescu, Degradation of pharmaceutical compound pentoxifylline in water by non-thermal plasma treatment, *Water Res.* 44 (2010) 3445–3453.
- [2] Y. Zhang, X. Xiong, Y. Han, H. Yuan, S. Deng, H. Xiao, F. Shen, X. Wu, Application of titanium dioxide-loaded activated carbon fiber in a pulsed discharge reactor for degradation of methyl orange, *Chem. Eng. J.* 162 (2010) 1045–1049.
- [3] T.C. Wang, N. Lu, J. Li, Y. Wu, Degradation of pentachlorophenol in soil by pulsed corona discharge plasma, *J. Hazard. Mater.* 180 (2010) 436–441.
- [4] P.S. Lang, D.M. Willberg, D.M., Oxidative degradation of 2,4,6-trinitrotoluene by ozone in an electrohydraulic discharge reactor, *Environ. Sci. Technol.* 32 (1998) 3142–3148.
- [5] E. Njatawidjaja, A.T. Sugiarto, T. Ohshima, M. Sato, Decoloration of electrostatically atomized organic dye by the pulsed streamer corona discharge, *J. Electrostat.* 63 (2005) 353–359.
- [6] L.R. Grabowski, E.M.V. Veldhuizen, A.J.M. Pemen, Corona above water reactor for systematic study of aqueous phenol degradation, *Plasma Chem. Plasma Process.* 26 (2006) 3–17.
- [7] C. Wang, Y. Wu, G. Li, Inactivation of *E. coli* with plasma generated by bipolar pulsed discharge in a three-phase discharge plasma reactor, *J. Electrostat.* 66 (2008) 71–78.
- [8] B. Sun, M. Sato, J.S. Clements, Oxidative processes occurring when pulsed high-voltage discharges degrade phenol in aqueous solution, *Environ. Sci. Technol.* 34 (2000) 509–513.
- [9] J. Li, M. Sato, T. Ohshima, Degradation of phenol in water using a gas-liquid phase pulsed discharge reactor, *Thin Solid Films* 515 (2007) 4283–4288.
- [10] D.R. Grymonpré, W.C. Finney, B.R. Locke, Aqueous phase pulsed streamer corona reactor using suspended activated carbon particles phenol oxidation: model data, *Chem. Eng. Sci.* 54 (1999) 3095–3105.
- [11] L.C. Lei, Y. Zhang, X.W. Zhang, Y.X. Du, Q.Z. Dai, S. Han, Degradation performance of 4-chlorophenol as a typical organic pollutant by a pulsed high voltage discharge system, *Ind. Eng. Chem. Res.* 46 (2007) 5469–5477.
- [12] C.M. Du, J.H. Yan, B.G. Cheron, Degradation of 4-chlorophenol using a gas-liquid gliding arc discharge plasma reactor, *Plasma Chem. Plasma Process.* 27 (2007) 635–646.
- [13] L. Wang, 4-Chlorophenol degradation and hydrogen peroxide formation induced by DC diaphragm glow discharge in an aqueous solution, *Plasma Chem. Plasma Process.* 29 (2009) 241–250.
- [14] D.M. Willberg, P.S. Lang, Degradation of 4-chlorophenol, 3,4-dichloroaniline, and 2,4,6-trinitrotoluene in an electrohydraulic discharge reactor, *Environ. Sci. Technol.* 30 (1996) 2526–2534.
- [15] W.F.L.M. Hoebe, E.M.V. Veldhuizen, W.R. Rutgers, C.A.M.G. Cramers, G.M.W. Kroesen, The degradation of aqueous phenol solutions by pulsed positive corona discharge, *Plasma Sources Sci. Technol.* 9 (2000) 361–369.
- [16] Y. Zhang, M. Zhou, X. Hao, L. Lei, Degradation mechanisms of 4-chlorophenol in a novel gas-liquid hybrid discharge reactor by pulsed high-voltage system with oxygen or nitrogen bubbling, *Chemosphere* 67 (2007) 702–711.
- [17] M. Tezuka, M. Iwasaki, Plasma-induced degradation of aniline in aqueous solution, *Thin Solid Films* 336 (2001) 204–207.
- [18] P. Lukes, M. Clupek, V. Babicky, V.J.P. Sunka, Generation of ozone by pulsed corona discharge over water surface in hybrid gas-liquid electrical discharge reactor, *J. Phys. D: Appl. Phys.* 38 (2005) 409–416.
- [19] J.S. Clements, Preliminary investigation of prebreakdown phenomena and chemical reactions using a pulsed high-voltage discharge in water, *IEEE Trans. Ind. Appl.* 23 (1987) 224–235.
- [20] B. Yang, M. Zhou, L. Lei, Synergistic effects of liquid and gas phase discharges using pulsed high-voltage for dyes degradation in the presence of oxygen, *Chemosphere* 60 (2005) 405–411.
- [21] A.T. Sugiarto, S. Ito, T. Ohshima, M. Sato, J.D. Skalny, Oxidative decoloration of dyes by pulsed discharge plasma in water, *J. Electrostat.* 58 (2003) 135–145.
- [22] A.A. Joshi, B.R. Locke, P. Arce, W.C. Finney, Formation of hydroxyl radicals, hydrogen peroxide and aqueous electrons by pulsed streamer corona discharge in aqueous solution, *J. Hazard. Mater.* 41 (1995) 3–30.
- [23] B. Sun, M. Sato, J.S. Clements, Optical study of active species produced by a pulsed streamer corona discharge in water, *J. Electrostat.* 39 (1997) 189–202.
- [24] J. Pawlat, S. Ihara, C. Yamabe, I. Polio, Oxidant formation and the decomposition of organic compounds in forming systems, *Plasma Process. Polym.* 2 (2005) 218–221.
- [25] W. Bian, X. Yin, J. Shi, Enhanced degradation of p-chlorophenol in a novel pulsed high-voltage discharge reactor, *J. Hazard. Mater.* 162 (2009) 906–912.
- [26] X. Lu, T. Pan, K. Liu, M. Liu, Radiation characteristics of plasma in a pulsed discharge in water, *J. Huazhong Univ. Sci. Tech.* 28 (2000) 85–87.
- [27] D. Hemmert, K. Shiraki, T. Yokoyama, S. Katsuki, H. Bluhm, H. Akiyama, Optical diagnostics of shock waves generated by a pulsed streamer discharge in water, in: *Pulsed Power Conference, 14th IEEE International*, vol. 1, 2003, pp. 232–235.
- [28] L.V. Lisitsyn, H. Nomiyama, S. Katsuki, H. Akiyama, Thermal process in a streamer discharge in water, *IEEE Trans. Dielectr. Electr. Insulat.* 6 (1999) 351–356.
- [29] X. Liu, C. Feng, Z. Zhu, Y. Xu, Z. Xu, Light radiation from pulsed discharges in water, *J. Beijing Inst. Technol.* 19 (1999) 8–12.