Effect of various gases and chemical catalysts on phenol degradation pathways by pulsed electrical discharges

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Abstract

The processes of phenol degradation by pulsed electrical discharges were investigated under several kinds of discharge atmospheres (oxygen, argon, nitrogen and ozone) and chemical catalysts (ferrous ion and hydrogen peroxide). The temporal variations of the concentrations of phenol and the intermediate products were monitored by HPLC and GC–MS, respectively. It has been found that the effect of various gases bubbling on phenol degradation rate ranked in the following order: oxygen-containing ozone > oxygen > argon > nitrogen. The high gas bubbling flow rate was beneficial to the removal of phenol. It was found that the degradation proceeded differently when in the presence and absence of catalysts. The phenol removal rate was increased when ferrous ion was added. This considerable enhancement may be due to the Fenton's reaction. What's more, putting the chemical additives hydrogen peroxide into the reactor led to a dramatic increase in phenol degradation rate. The mechanism was due to the direct or indirect photolysis and pyrolysis destruction in plasma channel. Furthermore, the intermediate products were monitored by GC–MS under three degradation conditions. More THBs were generated under degradation conditions without gases bubbling or adding any catalyst, and more DHBs under the condition of adding ferrous ion, and more carboxylic acids under the condition of oxygen-containing ozone gas bubbling. Consequently, three distinct degradation pathways based on different conditions were proposed.

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Keywords: Pulsed electrical discharge; Discharge atmosphere; Chemical catalyst; Intermediate product; Degradation pathway

1. Introduction

Over the past few decades, interest in the development of AOPs for the treatment of hazardous chemical water has grown enormously. A pulsed electrical discharge in gas and water treatment has attracted a great deal of attention from environmental scientists [1–9] and the discharge leads to both physical and chemical processes that directly or indirectly degrade organic compounds [3,10–13]. Clements et al. [1] investigated prebreakdown phenomena in water for point-plate geometries using high-voltage pulse. To one's surprise, the discharge characteristics were found to be extremely sensitive to those changes in the solution conductivity and the polarity and magnitude of the applied voltage. However, they did not propose a mechanism of dye breakdown. Sharma et al. [2] reported that pulsed streamer corona discharge in water was effective at breaking down phenol in aqueous solutions. Naturally, they speculated the possible degradation pathways. However, they did not determine the intermediates or discuss phenol degradation pathways. Sun et al. [14] found that the removal efficiency of organic contaminants in the aqueous solution was higher when it came to the spark discharge than to the streamer corona discharge, and it was greatly influenced by the discharge type and additives. Joshi et al. [3] and Grymonpré et al. [15] developed models including chemical reaction kinetics, and determined the rates of function of hydrogen peroxide, hydroxyl radicals and aqueous electrons by fitting the experimental data of phenol degradation to the model.

While progress has been made in understanding the effect of discharge characteristics, the chemical reaction kinetics and the reactor models, yet the correlations between the gaseous

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reagents, chemical catalysts, the aqueous degradation processes and the intermediate products in the aqueous phase have not been clarified. The specification of the gaseous reagents and chemical catalysts that are decisive in the aqueous phenol degradation and its oxidizing efficiency is of great importance not only in understanding the streamer corona-induced degradation process, but also in developing pulsed electrical discharge reactors for industrial implementation. Moreover, it is important to ensure that the reduced phenols are not converted into toxic materials in wastewater treatment. However, the final byproducts and the reaction mechanisms involved in the destruction of organic compounds by pulsed electrical discharge have not been sufficiently clarified up until now.

In this paper, we focused on the influence of discharge atmospheres (oxygen, argon, nitrogen and ozone) and chemical additives (ferrous ion and hydrogen peroxide) on the phenol degradation in the aqueous phase. The temporal variations of the concentrations of phenol and the intermediate products were monitored by HPLC and GC–MS, respectively. Most of the intermediate products and the final byproducts were identified and three distinct reaction pathways were proposed.

2. Materials and methods

2.1. High-voltage power supply and streamer corona reactor

As presented in Fig. 1, in the high-voltage pulse generator the high-voltage alternating input current first goes through a series of high-voltage current-limiting resistors. A series of diodes are used to full-wave rectify the alternating current. Upon that, the charge is then stored in a bank of capacitors that are connected to a rotating spark gap. When a rotating rod in the spark gap links with two opposing copper electrodes (one attached to the capacitors and the other attached to the reactor), the charge stored in the capacitors is discharged across the spark gap, resulting in a pulsed discharge delivered into the liquid phase reactor. The rotating rod in the spark gap links with the two copper electrodes twice for each full rotation.

The reactor is a cylindrical plexiglass tube with dimensions of 50 mm inside diameter and 256 mm in length. Pulsed electrical discharge treatment of the test solution is provided by non-uniform point-to-plate electrode. Seven stainless steel hypodermic needles are inserted into the reactor from the bottom, through silicone sealing insulation. The needles are con-
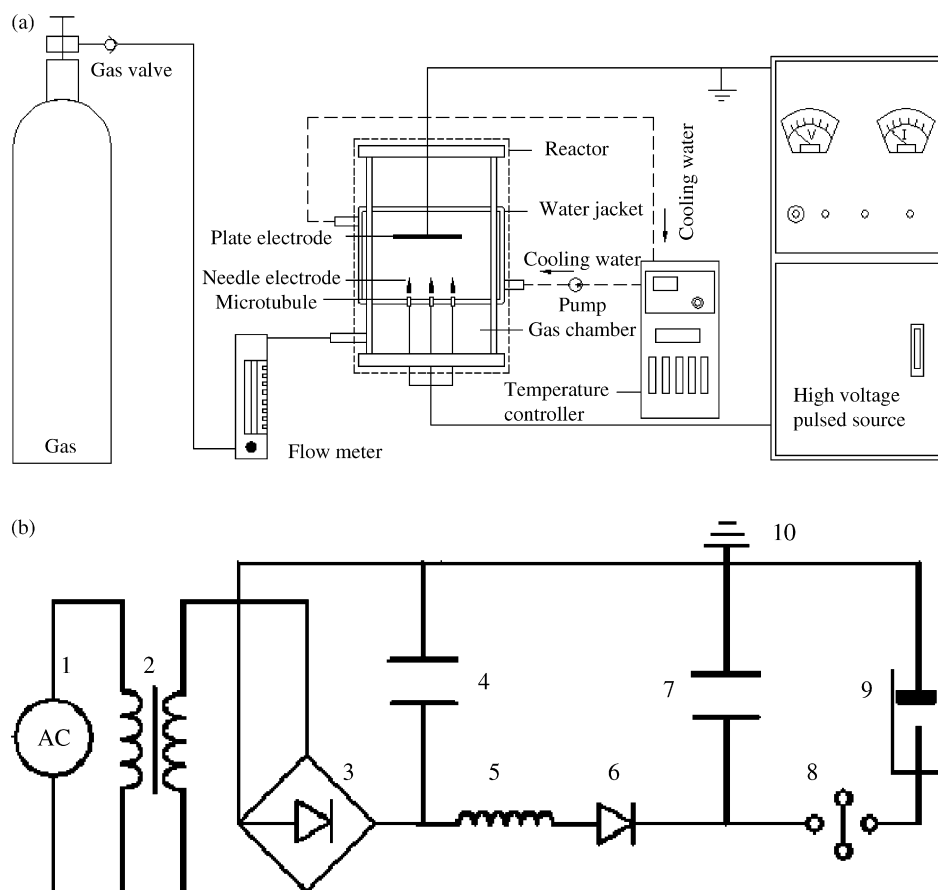

Fig. 1. (a) The diagrammatic sketch of experimental apparatus. (b) The topology circuit of pulsed high voltage source. (1) AC power; (2) high voltage transformer; (3) silicon rectifier; (4) filter and storage capacitor; (5) current-limiting resistor; (6) diode; (7) pulse forming capacitor; (8) spark gap; (9) reactor; (10) grounding.

nected to the high voltage and the stainless steel around plate ground electrode is placed at the top of the reactor opposite to the high voltage discharge electrode.

2.2. Gas handling system and sample measurement system

Oxygen or nitrogen or argon from gas cylinder passed through silica gel, carbon and molecular sieve columns for purification. Ozone was generated with an ozone generator with a flow of 200 mL/min. Ozone concentration in the gas phase was analyzed by iodometric method [16]. Phenol was of analytical grade, and the initial concentration of phenol was 50 mg/L. Doubly distilled water was used in this study. The liquid conductivity was measured by conductivity gauge (DDS-11 A) and pH value of the solution by pH meter (pHS-25). The liquid conductivity was adjusted to 10 μS/cm by adding HCl or KOH. The initial pH was 6.5 and the temperature was 15 °C. The concentration of phenol was measured by using HPLC (Knauer K-2005), equipped with a MS-2 C18 column (Ø 4.6 mm × 250 mm) and a UV detector. An aqueous solution consisting of 70% phosphoric acid (0.01 M H_3PO_4) and 30% acetonitrile was used as the eluting solvent.

Intermediates produced in the phenol degradation were analyzed by the following procedure. The sample of treated solution was first extracted for 2 h using 100 mL of dichloromethane. The organic extract was then concentrated to small volume by flowing N_2. Subsequently the sample was analyzed using Thermo Quest Trace GC2000/Trace MS with HP-5 column. The intermediates were identified by matching with the standard samples, considering both elution time and mass spectrum.

3. Results and discussion

3.1. Mechanism and effect of various gases bubbling on phenol degradation

In order to investigate the role of different gases bubbling in degrading phenol, oxygen, nitrogen, oxygen gas-containing ozone and an inert gas (argon) were bubbled separately through the hypodermic needle electrode. Fig. 2 shows the experimental results for the removal of phenol by pulsed electrical discharge with the various gases bubbling in the solution.

As shown in Fig. 2, the degradation rates under oxygen gas and oxygen-containing ozone bubbling were much faster than those under nitrogen and argon gas bubbling and without gas bubbling. The probable reason that the removal efficiency was higher with oxygen gas bubbling than with argon gas bubbling was that, in the case of with oxygen gas bubbling in pulsed electrical discharge, not only lots of •OH radicals were produced to degrade phenol, but also other species such as ozone, or superoxide (O_2^-) and singlet oxygen ($^1O_2$), participated in the chemical reactions. In contrast, when pulsed electrical discharges took place in an argon atmosphere over an oxygen-free phenol solution, the argon ions and metastables created by pulsed electrical discharges will dissociate water molecules to produce hydroxyl radicals (and hydrogen atoms), but no ozone or O atoms can be formed [17]. So the degradation rate under the oxygen atmosphere was much higher than that under the argon one.
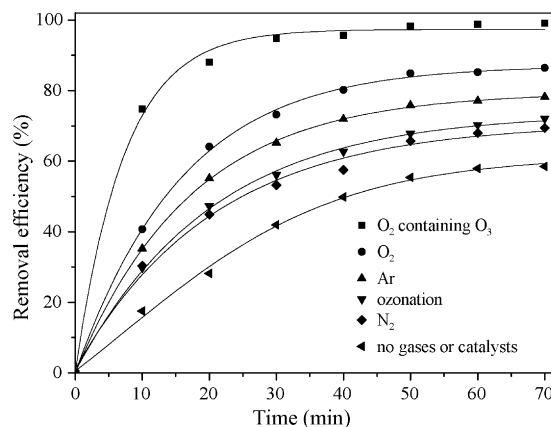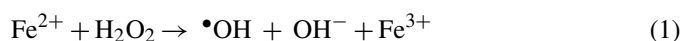

Fig. 2. Phenol concentration as a function of the treatment time at $V = 25$ kV, $f = 60$ Hz, $d = 30$ mm, [Phenol]$_0$ = 50 mg/L, [O_2] = [N_2] = [Ar] = 200 mL/min, [O_3] = 1.5 M, for the oxidation of phenol in aqueous solution by pulsed electrical discharges with gases bubbling.

By comparing with the results of oxygen bubbling and nitrogen bubbling, one may notice that oxygen bubbling performed better than nitrogen bubbling. The probable reason was that the dissociation of oxygen molecules occurs at a lower reduced-electrical-field intensity around the plasma channel and it requires less energy than that of the dissociation of nitrogen molecules. Furthermore, high-energy electrons are typically considered to react primarily with molecular oxygen, resulting in efficient production of hydroxyl radicals and the formation of ozone, an additional active species [18]. Therefore, the degradation efficiency with oxygen gas bubbling was faster than that under nitrogen bubbling. Nitrates and other nitrogen oxides were measured in the experiments with nitrogen gas bubbling. The concentration of nitrite ion increased to 0.09 mM at first 5 min and then decreased while the concentration of nitrate ion increased tardily to 0.17 mM at 30 min.

The combined action of oxygen-containing ozone with pulsed electrical discharges was more effective in decomposing organic pollutants in water as compared with pulsed electrical discharges with oxygen bubbling or just the former one only. It may be due to the enhancement in ozone decomposition by pulsed electrical discharges in water, thus the rate of ozone transferring into water should increase. Therefore, phenol removal in combination with pulsed discharges and ozonation in water increased.

3.2. Mechanism and effect of adding Fe^{2+} on phenol degradation

It is necessary to study the effects of other compounds existing in the aqueous solution on phenol degradation. In Fig. 3, it can be seen that a dramatic increase of phenol degradation rate occurred upon adding ferrous ion to the reactor. The rapid increase in the reaction rate upon the addition of ferrous ion may be attributed to the presence of Fenton's reaction and Hamilton's reaction. In the presence of Fe^{2+}, the following process should be added [19,20]:
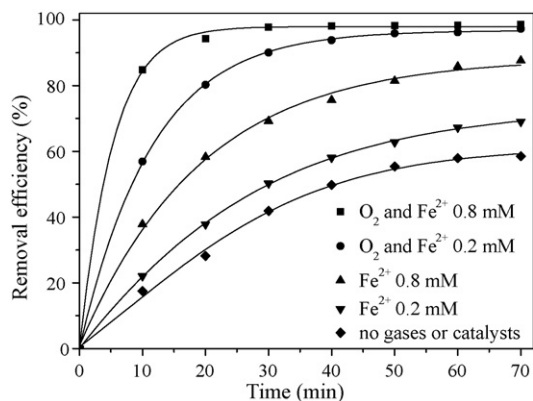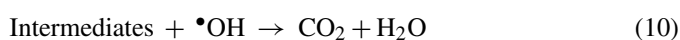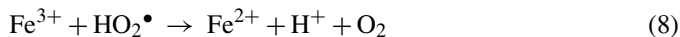
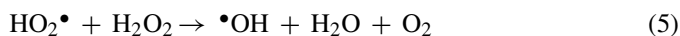$$Fe^{2+} + H_2O_2 \rightarrow {}^•OH + OH^- + Fe^{3+} \qquad (1)$$

Fig. 3. Phenol concentration as a function of the treatment time at $V = 25\,kV$, $f = 60\,Hz$, $d = 30\,mm$, [Phenol]$_0$ = 50 mg/L, [O$_2$] = 200 mL/min, when [Fe^{2+}] was 0.2 and 0.8 mM, the liquid conductivity was 67 and 242 µS/cm, for the oxidation of phenol in aqueous solution by pulsed electrical discharges in the presence of ferrous sulfate.

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+ \leftrightarrow Fe^{2+} + {}^\bullet HO_2 + H^+ \tag{2}$$

$$Fe^{3+} + OH^- \rightarrow Fe(OH)^{2+} \leftrightarrow Fe^{2+} + {}^\bullet OH \tag{3}$$

$${}^\bullet OH + H_2O_2 \rightarrow HO_2{}^\bullet + H_2O \tag{4}$$

$$HO_2{}^\bullet + H_2O_2 \rightarrow {}^\bullet OH + H_2O + O_2 \tag{5}$$

$$HO_2{}^\bullet + HO_2{}^- \rightarrow {}^\bullet OH + OH^- + O_2 \tag{6}$$

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^- \tag{7}$$

$$Fe^{3+} + HO_2{}^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \tag{8}$$

$$Phenol + {}^\bullet OH \rightarrow Intermediates \tag{9}$$

$$Intermediates + {}^\bullet OH \rightarrow CO_2 + H_2O \tag{10}$$
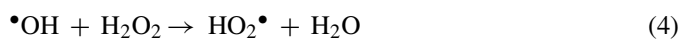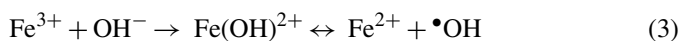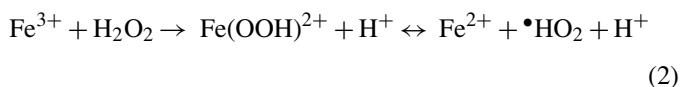
The hydroxyl radical can again combine with Fe^{2+} to produce the hydroxide ion. In the presence of larger concentrations of an organic compound, hydroxyl radicals may preferentially react with the organic compounds rather than Fe^{2+} [21].

3.3. Mechanism and effect of adding H$_2$O$_2$ on phenol degradation

Fig. 4 shows the degradation of phenol by pulsed electrical discharge in the presence of hydrogen peroxide. It can be observed that a dramatic increase of phenol degradation rate occurred upon adding hydrogen peroxide to the solution. Since the reaction of phenol with hydrogen peroxide is very slow at the ambient temperature, the degradation process may be due to the reaction of hydroxyl radicals produced by photolysis of hydrogen peroxide, which was caused by UV radiation from electrical discharge plasma.

The chemical effects of the electrical discharge plasma are due to direct photolysis (the electrical discharge plasma only), indirect photolysis (combination of chemical additives and the
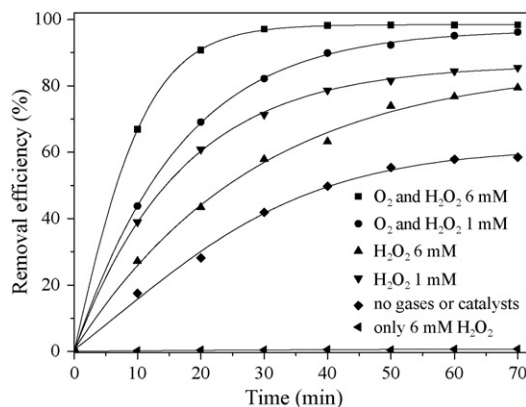

Fig. 4. Phenol concentration as a function of the treatment time at $V = 25\,kV$, $f = 60\,Hz$, $d = 30\,mm$, [Phenol]$_0$ = 50 mg/L, [O$_2$] = 200 mL/min, for the oxidation of phenol in aqueous solution by pulsed electrical discharges with H$_2$O$_2$.

electrical discharge plasma) and pyrolysis destruction in plasma channels [4]. The photolysis could be due to the UV radiation. A part of vacuum UV in the region of the spectrum $\lambda = 75$–185 nm is absorbed by the water layer around the plasma channels [22], but the UV region of the spectrum $\lambda > 185$ nm expands into the bulk of solution, and then it reacts with organic contaminants in aqueous solution. This process has been described in many literatures [14]:

$$H_2O_2 + h\nu \rightarrow {}^\bullet OH + {}^\bullet OH \tag{11}$$

In this equation, 1 mol of H$_2$O$_2$ produces 2 mols of hydroxyl radicals by UV light. Therefore, a large number of hydroxyl radicals are produced in the reactor, the effective degradation of organic contaminants may occur in aqueous solution.

3.4. Intermediate products and a discussion of the degradation pathways

In order to obtain the comprehensive profile of phenol degradation by pulsed electrical discharge, a series of experiments were carried out to determine the intermediates. We investigated the degradation under three conditions, without gases bubbling or adding any catalyst, with adding ferrous ion and with oxygen-containing ozone gas bubbling. All the intermediate products and their retention time monitored by GC–MS are shown in Table 1.

Firstly, we investigated phenol degradation under normal condition, that was, without gas bubbling or adding any catalyst. The main intermediate products were formic acid (1.94 min), acetic acid (3.11 min), oxalic acid (3.18 min), *p*-benzoquinone (5.50 min), phenol (6.31 min), pyrocatechol (9.38 min), hydroquinone (9.74 min), pyrogallol (11.74 min), hydroxyhydroquinone (12.13 min). THBs were detected in considerable amount besides the intermediate products mentioned above. The probable reaction pathway was as follows.

The ${}^\bullet OH$ radical reacts with phenol to form the dihydroxycyclohexadienyl radical ${}^\bullet C_6H_5(OH)_2$ (DHCHD) as follows [23]:

$$C_6H_5(OH) + {}^\bullet OH \rightarrow {}^\bullet C_6H_5(OH)_2 \tag{12}$$
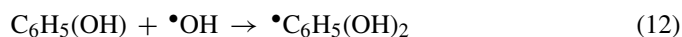
Table 1
The retention time (t_R) of the standard compounds in the phenol oxidation product mixture obtained from GC–MS profiles

GC–MS t_R (min)	Identity	Formula	a	b	c
1.55 ± 0.01	Glyoxal	OHC—CHO			+
1.94 ± 0.01	Formic acid	HCOOH	+	+	+
2.42 ± 0.01	Glyoxylic acid	HOOC—CHO			+
3.11 ± 0.01	Acetic acid	CH_3COOH	+	+	+
3.18 ± 0.01	Oxalic acid	HOOC—COOH	+	+	+
4.00 ± 0.01	Malonic acid	$C_3H_4O_4$		+	+
4.69 ± 0.01	Maleic acid	$C_4H_4O_4$		+	+
4.79 ± 0.01	Metacetonic acid	$C_3H_6O_2$			+
5.32 ± 0.01	cis,cis-Muconic acid	$C_6H_6O_4$		+	+
5.50 ± 0.01	p-Benzoquinone	$C_6H_4O_2$	+	+	+
6.31 ± 0.01	Phenol	C_6H_6O	+	+	+
9.39 ± 0.01	Pyrocatechol	$C_6H_6O_2$	+	+	+
9.75 ± 0.01	Hydroquinone	$C_6H_6O_2$	+	+	+
11.74 ± 0.01	Pyrogallol	$C_6H_6O_3$	+	+	
12.13 ± 0.01	Hydroxyhydroquinone	$C_6H_6O_3$	+	+	

The presented values are averages together with their 95% confidence interval. (a) Without any gas bubbling or adding chemical catalysts, (b) in the presence of Fe^{2+} and (c) under conditions of oxygen-containing ozone gas bubbling; (+) the compounds that were detected by GC–MS; t_R represents retention time.

The DHCHD can decay to form the phenoxyl radical $C_6H_5O^\bullet$. The phenoxyl radical $C_6H_5O^\bullet$ reacts with the $^\bullet OH$ radical to form DHBs.

$$C_6H_5O^\bullet + {}^\bullet OH \rightarrow C_6H_4(OH)_2 \tag{13}$$

In the process of phenol degradation by pulsed electrical discharge without gas bubbling or adding any additives, THBs were detected in much greater amount than those in the presence of Fe^{2+} and with gases bubbling or adding any additives. From the experiment, it was found that, the results of the degradation were in agreement with that of Tezuka in contact glow discharge electrolysis [24], and due to the electron-donating character of the phenolic —OH group and the electrophilicity of the radical, the predominant hydroxylation products are pirogal, hydroxyhydroquinone, o-dihydroxybenzene and p-dihydroxybenzene [24].

Fleszar and Ploszynska also reported that when electrical discharge takes place in water without gases bubbling or adding any catalysts, $^\bullet OH$ radical was mainly caused by the electrophilic attack and was produced by the liquid phase discharge directly in water, so the concentration of the aqueous hydroxyl radicals is lower, and the formation of benzene trihydroxyderivatives is an essential process considering that trihydroxybenzenes are easily oxidized to ring destruction product. The THBs were detected in considerable amounts [25].

The intermediate products are easy to be further oxidized under the action of the radicals. The opening of the aromatic ring leads to the formation of low molecular weight compounds, mainly organic acids. In addition, the intermediate products or organic acids are also oxidized through hydroxylation and hydration, finally forming carbon dioxide. No other gaseous phenol oxidation products such as carbon monoxide have been obtained.
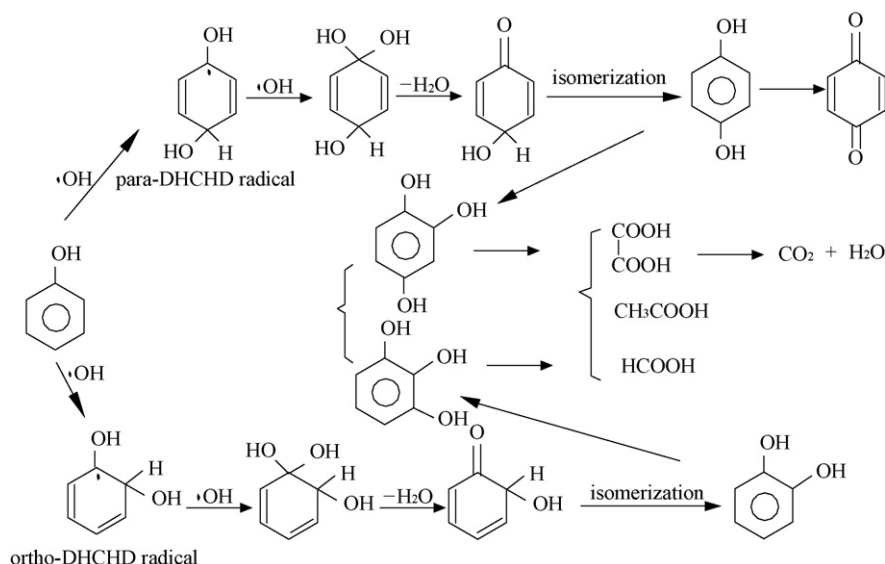

Fig. 5. Degradation pathways of phenol by pulsed electrical discharges under conditions without any gas bubbling or adding chemical catalysts. $V = 25\,kV$, $f = 60\,Hz$, $d = 30\,mm$, $[Phenol]_0 = 50\,mg/L$.

Even if carbon monoxide is produced, it will be rapidly converted to carbon dioxide on account of oxides. Fig. 5 shows the degradation pathway of phenol by pulsed electrical discharge under normal condition [24].

Secondly, we investigated phenol degradation under the condition of adding ferrous ion. It can be seen that in the presence of Fe^{2+}, the major intermediates were formic acid (1.94 min), acetic acid (3.11 min), oxalic acid (3.18 min), malonic acid (4.00 min), maleic acid (4.69 min), cis,cis-muconic acid (cis,cis-1,3-butadiene-1,4-dicarboxylic acid: HOOC–CH=CH–CH=CH–COOH) (5.32 min), p-benzoquinone (5.50 min), phenol (6.31 min), pyrocatechol (9.38 min), hydroquinone (9.74 min), pyrogallol (11.74 min), hydroxyhydroquinone (12.13 min).

When the reaction was carried out in the presence of Fe^{2+}, hydrogen peroxide was decomposed to produce large numbers of hydroxyl radicals through Fenton's reaction, but no ozone and

O atoms can be formed. Hydroxylation of phenol was the main degradation pathway. DHBs and benzoquinone were found in much greater amount than those in terms of electrical oxidation in oxygen and the case without adding any catalyst. In contrast, the concentrations of hydroxyhydroquinone and pyrogallol were very low. The probable reason was that when the concentration of hydroxyl radicals was very high, DHBs degrade in two competitive ways. When the hydroxyl groups are the sites of the initial step they will be oxidized to yield benzoquinones. When the aromatic rings are the sites of attack they will produce trihydroxylderivatives. It appears that the former is the predominant one [26]. Therefore, the production of DHBs was significant. The differences in the amount of polyhydroxybenzenes present brought about the color difference between the oxidized solutions. Fig. 6a shows the degradation pathway of phenol by pulsed electrical discharge in the presence of Fe^{2+} [27].

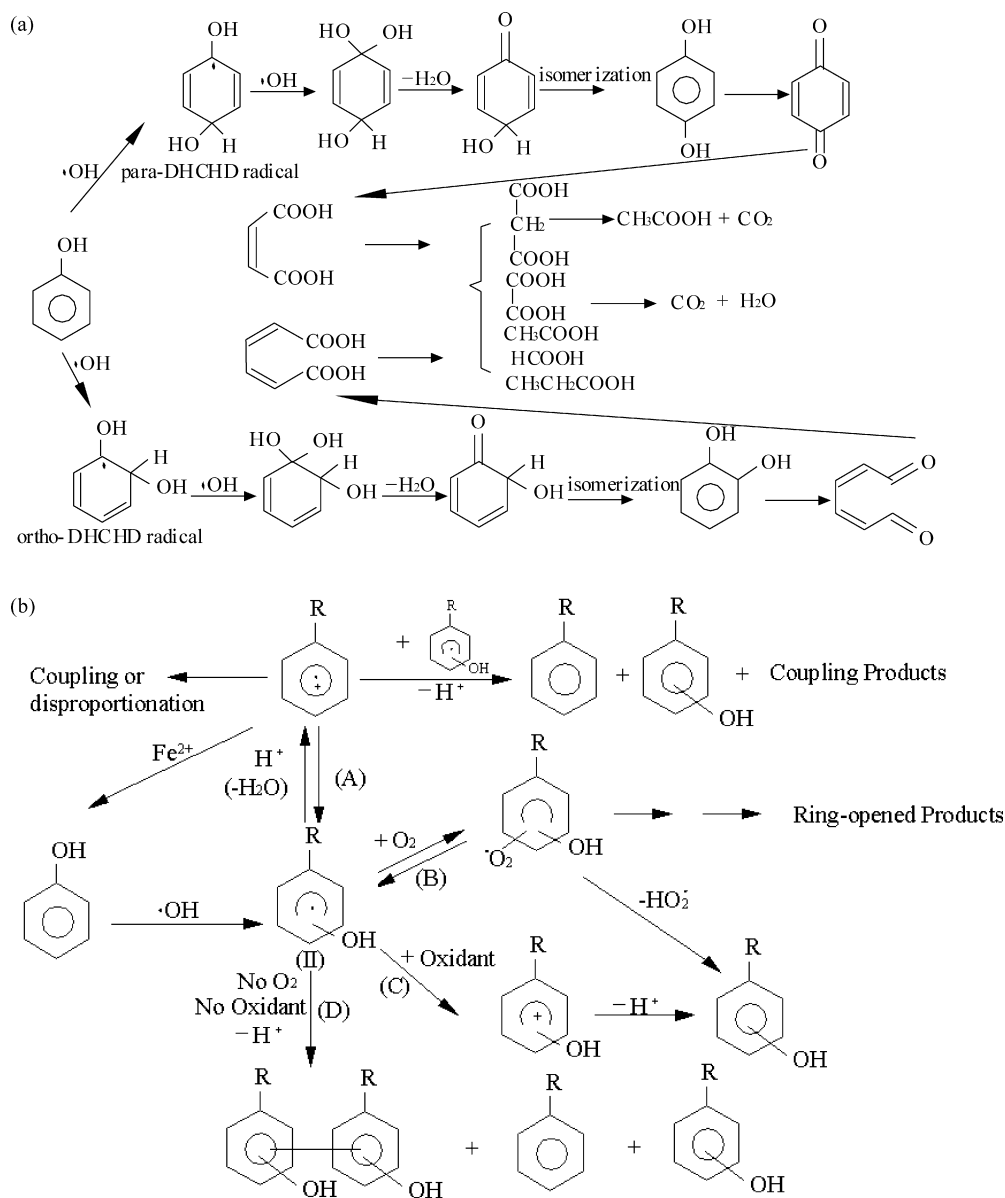Fig. 6. Degradation pathways of phenol by pulsed electrical discharges in the presence of Fe^{2+}. $V = 25$ kV, $f = 60$ Hz, $d = 30$ mm, [Phenol]$_0 = 50$ mg/L.

Another degradation pathway of phenol by $^\bullet$OH radical in the presence of Fe^{2+} is shown in Fig. 6b [28]. Depending on pH and availability of suitable oxidants or reductants, **II** may react further by: acid-catalyzed elimination of water to form a radical cation (path A); formation of a dioxygen radical adduct (path B); oxidation to a cyclohexadienyl cation (path C); or-when paths B and C are unavailable-coupling and disproportionation (path D).

Thirdly, we investigated phenol degradation under the condition of oxygen-containing ozone gas bubbling. The main intermediate products were glyoxal (1.55 min), formic acid (1.94 min), glyoxylic acid (2.42 min), acetic acid (3.11 min), oxalic acid (3.18 min), malonic acid (4.00 min), maleic acid (4.69 min), *cis,cis*-muconic acid (5.32 min), metacetonic acid (4.79 min), *p*-benzoquinone (5.50 min), phenol (6.31 min), pyrocatechol (9.38 min), hydroquinone (9.74 min). The results were more complex with oxygen bubbling than without gas bubbling and in the presence of Fe^{2+}. Glyoxal and glyoxylic acid were

found. The carboxylic acids were found in much greater amount than those in terms of electrical oxidation under normal condition and in the presence of ferrous ion. The reason was that phenol degradation by pulsed electrical discharge with oxygen bubbling was by not only hydroxylation, but also direct and indirect ozonation.

Fig. 7 shows the mechanism of phenol degradation by pulsed electrical discharge with oxygen gas bubbling. When pulsed electrical discharge took place without gases bubbling or in the presence of Fe^{2+}, the mechanism of phenol degradation was mainly caused by the electrophilic attack of the $^\bullet$OH radical produced by the liquid phase discharge directly in water, and the hydroxylation of phenol was the main degradation pathway. In contrast, phenol degradation by pulsed electrical discharge with oxygen bubbling was not only the action of the $^\bullet$OH radicals formed through the electron impact of H_2O molecules in the water vapor, but also direct and indirect ozonation, and the action of peroxone process through the reaction of dissolved

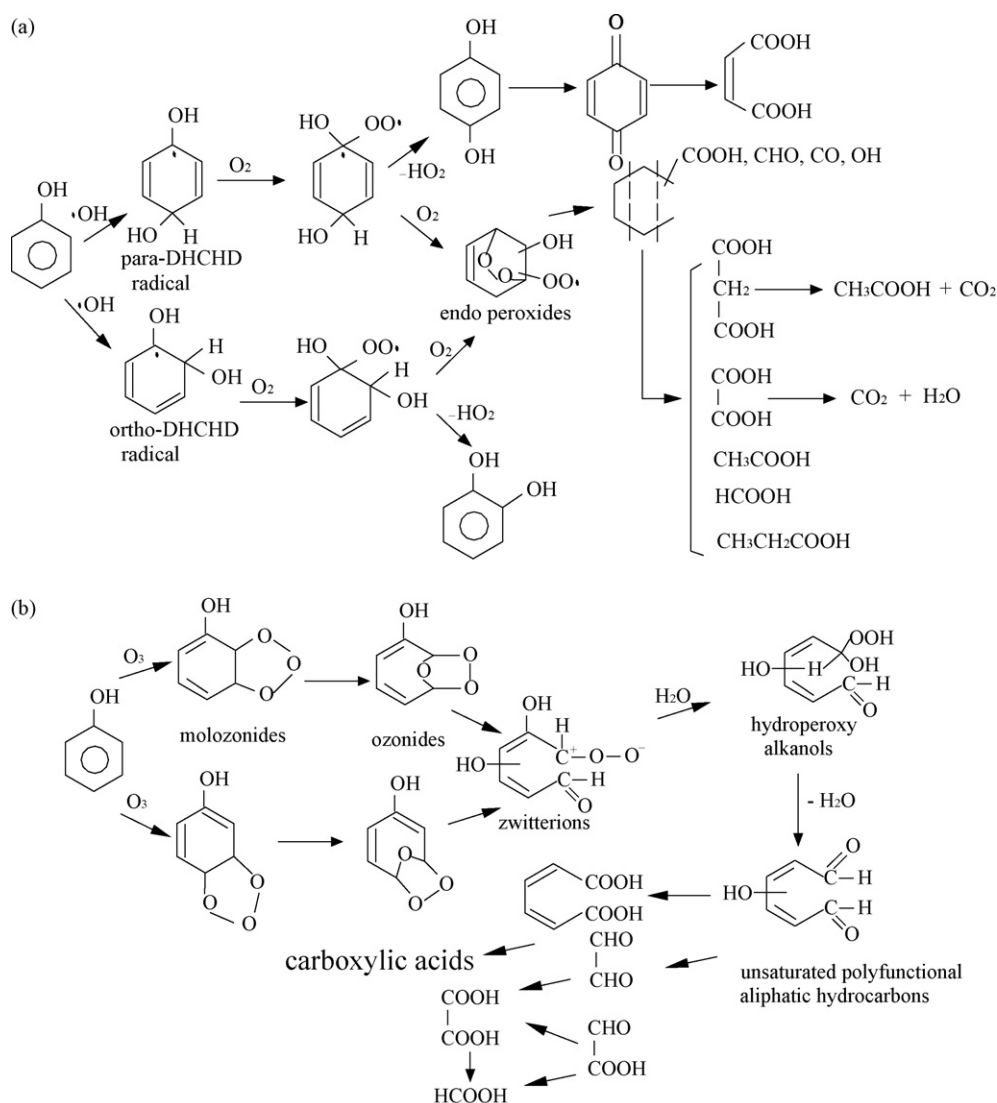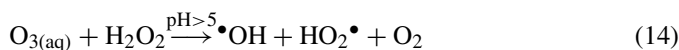Fig. 7. Degradation pathways of phenol by pulsed electrical discharges under conditions of oxygen-containing ozone gas bubbling. $V = 25$ kV, $f = 60$ Hz, $d = 30$ mm, $[Phenol]_0 = 50$ mg/L. (a) Attack of oxygen on phenol; (b) ozone addition to phenol.

ozone with aqueous hydrogen peroxide [29–31].

$$O_{3(aq)} + H_2O_2 \xrightarrow{pH>5} {}^\bullet OH + HO_2{}^\bullet + O_2 \tag{14}$$

Under an oxygen gas bubbling with pulsed electrical discharge, Lukes reported that under this case, the formation of gaseous ozone was very important, and it dominated over the formation of the $^\bullet$OH radicals, and the contribution of the gas phase discharge in this case was determined mainly by the dissolution of gaseous ozone into the water and its subsequent interaction with phenol [29]. In water, ozone may react with dissolved substances, or it may decompose to form secondary oxidants such as $^\bullet$OH radicals, which then themselves immediately react with the solutes. From the above, it can be seen that the degradation of phenol by pulsed electrical discharge under oxygen bubbling is mainly caused by direct and indirect oxidation of ozone, and the main effect of phenol degradation was dependent on ozonation. Comparing with literatures about ozonation [32–37], we can see that the intermediates of phenol degradation by ozonation or pulsed electrical discharge with oxygen gas bubbling were similar. They were pyrocatechol, hydroquinone, glyoxal, formic acid, glyoxylic acid, acetic acid, oxalic acid, malonic acid, maleic acid, *cis,cis*-muconic acid, metacetonic acid, *p*-benzoquinone. The difference between pulsed electrical discharge with oxygen gas bubbling and pure ozonation was that $^\bullet$OH radicals, UV, ultrasonic and hydrogen peroxide were produced in addition to O_3 during the high voltage pulsed electrical discharge in water with oxygen gas bubbling. Furthermore, $^\bullet$OH radicals were formed through the electron impact of H_2O molecules in the water vapor, and more $^\bullet$OH radicals were produced through the synthetic effect of photolysis and pyrolysis. Therefore, the degradation efficiency of phenol by pulsed electrical discharge with oxygen bubbling was better than that of only ozonation.

As mentioned above about phenol degradation by pulsed electrical discharge, the $^\bullet$OH radical reacts with phenol to form DHCHD. Under the circumstance of oxygen, oxygen will attack these radicals to produce dihydroxycyclohexadienylperoxyl (DHCHDP) radicals. The DHCHDP radical may decay in a first-order process to form catechol by elimination of a hydroperoxyl radical ($^\bullet HO_2$) [38].

$$^\bullet C_6H_5(OH)_2 + O_2 \rightarrow {}^\bullet C_6H_5(OH)_2O_2$$
$$\rightarrow C_6H_4(OH)_2 + {}^\bullet HO_2 \tag{15}$$
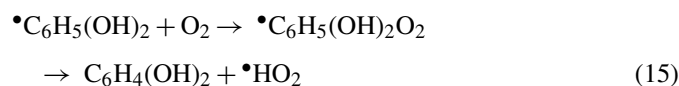
DHCHDP form endoperoxides through repeated scavenges of oxygen. These very instable intermediates are decomposed by ring cleavage.

The intermediate products are easily oxidized further under the action of the radicals and oxygen. The opening of the aromatic ring leads to the formation of low molecular weight compounds, mainly organic acids. The intermediate products or organic acids can also be oxidized through hydroxylation and hydration, finally forming carbon dioxide. Fig. 7a shows the degradation pathway of phenol by pulsed electrical discharge in the presence of oxygen [32–35,39].

Among possible chemically active species, ozone was expected to be the very important species. Large numbers of ozone were produced in the process of pulsed electrical discharge with oxygen bubbling. Molecular ozone selectively reacts with contaminants through cyclo-addition and electrophilic reactions with unsaturated aromatic and aliphatic species. In the oxidation of phenol by molecular ozone, it has been proposed that electrophilic attack by ozone leads to formation of the hydroxylated products as the major intermediates [40]. On the other hand, 1,3 dipolar cyclo-addition of ozone causes direct ring cleavage of phenol producing muconic acid or muconaldehyde. These ring-cleavage products have dual-carbon bonds and undergo further ozonation that yields organic acids [41]. Fig. 7b shows direct ozone attack on phenol to invoke ring opening by cyclo-addition [32–35,39].

Ozone decomposition is complicated in water: many transient oxidizing species ($^\bullet$OH, $^\bullet HO_2$, O^-, $O_3{}^-$, $^\bullet$O and singlet $^1O_2$) are suggested by the literatures [42,43]. These species are highly reactive, which may account for the effectiveness of ozone in destroying organic contaminants. In this way, a complex mixture of unsaturated and saturated aliphatic C_1–C_6 hydrocarbons was produced, having polyfunctional groups such as carboxyl, aldehyde, ketone and alkanol groups. Glyoxal, glyoxylic acid may result from multifold attack of ozone on phenol. Formic acid may be produced by carbon monoxide loss from glyoxylic acid or decarboxylation of oxalic acid.

From the chromatograph area of each intermediate product in GC–MS profiles, we can see that more THBs were generated under degradation conditions without gases bubbling or adding any catalyst, and more DHBs when adding ferrous ion, and more carboxylic acids when oxygen-containing ozone gas bubbling.

4. Conclusion

In the degradation of phenol by pulsed electrical discharge, the effect of various gases bubbling on degradation rate ranked in the following order: oxygen-containing ozone > oxygen > argon > nitrogen. The high gas bubbling flow rate was beneficial to the removal of phenol.

The degradation proceeded differently when in the presence and absence of catalysts. The phenol removal rate can be increased when ferrous ion was added. This considerable enhancement may be due to the Fenton's reaction. The addition of a small amount of hydrogen peroxide greatly increased the degradation rate of phenol. The mechanism behind the increase of the degradation rate was due to the direct or indirect photolysis and pyrolysis destruction in plasma channel.

The intermediate products were monitored by GC–MS under three degradation conditions. Identified products were glyoxal, formic acid, glyoxylic acid, acetic acid, oxalic acid, malonic acid, maleic acid, *cis,cis*-muconic acid, metacetonic acid, *p*-benzoquinone, pyrocatechol, hydroquinone, pyrogallol, hydroxyhydroquinone. More THBs were generated under degradation conditions without gas bubbling or adding any catalyst, and more DHBs when adding ferrous ion, and more carboxylic acids when oxygen-containing ozone gas bubbling.

Consequently, the degradation pathways based on conditions above were in great difference.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2007.05.024.

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