Use of a pulsed high-voltage discharge for removal of organic compounds in aqueous solution

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Abstract. Results obtained using a pulsed-streamer corona discharge for organic compound removal are reported in this investigation. The removal of phenol and the effects of various parameters on the removal efficiency were studied. The intermediate products and final byproducts were also studied. It was found that the organic contaminants in aqueous solution could be destroyed effectively by the pulsed-streamer corona discharge and that the organic compound removal was greatly influenced by gas injection (bubbling). In addition, a preliminary study of the reaction mechanism was performed. Byproducts were determined for phenol removal. The main intermediate products produced by the pulsed-voltage discharge during the treatment process were hydroquinone, pyrocatechol and 1,4-benzoquinone. These intermediate products disappeared when the residence time was increased. By analysing the total carbon content of the treated phenol solution, it was found that 83% of the total organic carbon was removed without oxygen bubbling and 86% was removed with oxygen bubbling. Carbon dioxide emitted in the gas phase was measured by an absorption method.

1. Introduction

Several methods have been proposed and/or are currently used to remove hazardous chemicals from contaminated waters. For example, oxidation using ozone [1], high-energy electron irradiation [2], carbon absorption [3] and advanced oxidation processes (AOPs) are considered to be promising alternatives for the treatment of pollutants [4]. High-energy electron irradiation has been used to treat organic compounds [2, 5]. Electrical discharges produced by pulsed high-voltage is a new method developed recently which has been used to degrade organic pollutants in waste water [6–8], because not only is the hydroxyl radical produced, but also atomic oxygen (which has a high oxidation potential) [9].

The most effective way of oxidizing organics is to use chemical reactants, i.e. reactants with a high oxidizing potential, such as $\cdot OH$, $\cdot O$, O_3 and H_2O_2. Since the most powerful oxidizing species are in fact the hydroxyl radical, followed by atomic oxygen and ozone, the active species $\cdot OH$, $\cdot O$, O_3 and H_2O_2 are important reactants. Especially, the OH radical is known to play an important role in oxidative purification of water and degrading organic compounds [17, 18].

As was discussed in our previous investigations [9, 10], the pulsed discharge makes it possible to instantaneously form a strong electric field and also to produce a non-thermal plasma in which various active species ($\cdot OH$, $\cdot H$, $\cdot O$, $^1O_2$, $\cdot HO_2$, O_2^-, H_2O_2, O_3, etc) exist. The production of active

species such as $\cdot OH$, H_2O_2 and O_3 in water or aqueous solutions has also been studied using a pulsed-streamer corona discharge [11, 12]. In addition, the effects of the streamer-corona discharge parameters on radical formation have been investigated [9]. The initial reaction rate constants for the formation of hydroxyl radicals, hydrogen peroxides and aqueous electrons produced by pulsed-streamer corona discharges were determined by Joshi *et al* [13]. Regarding the application of radicals, the degradation of phenol in aqueous solution was studied by Sharma *et al* [6] using a pulsed-streamer corona discharge. A combination of air stripping and pulsed corona was used to remove trihalomethane from water, as reported by Ai-Arainy *et al* [14] and Lubicki *et al* [15]. Goheen *et al* [16] described a process in which a direct current (DC) corona discharge was created between an electrode and the liquid–waste surface. It was observed that a variety of waste water contaminants could be destroyed using this reactor. All these previous investigations of the removal of organics were based on studies of the experimental conditions, which affect the removal. The final products formed in the discharge and the organic compound removal mechanism have not been studied in detail.

The transformation of organic compounds by radicals is of great practical importance not only in the oxidative purification of water, but also in the processing of industrial water with ozone where part of the saturated organic material that is present in trace amounts is degraded to low-molecular-weight carboxylic and dicarboxylic acids [17]. In this
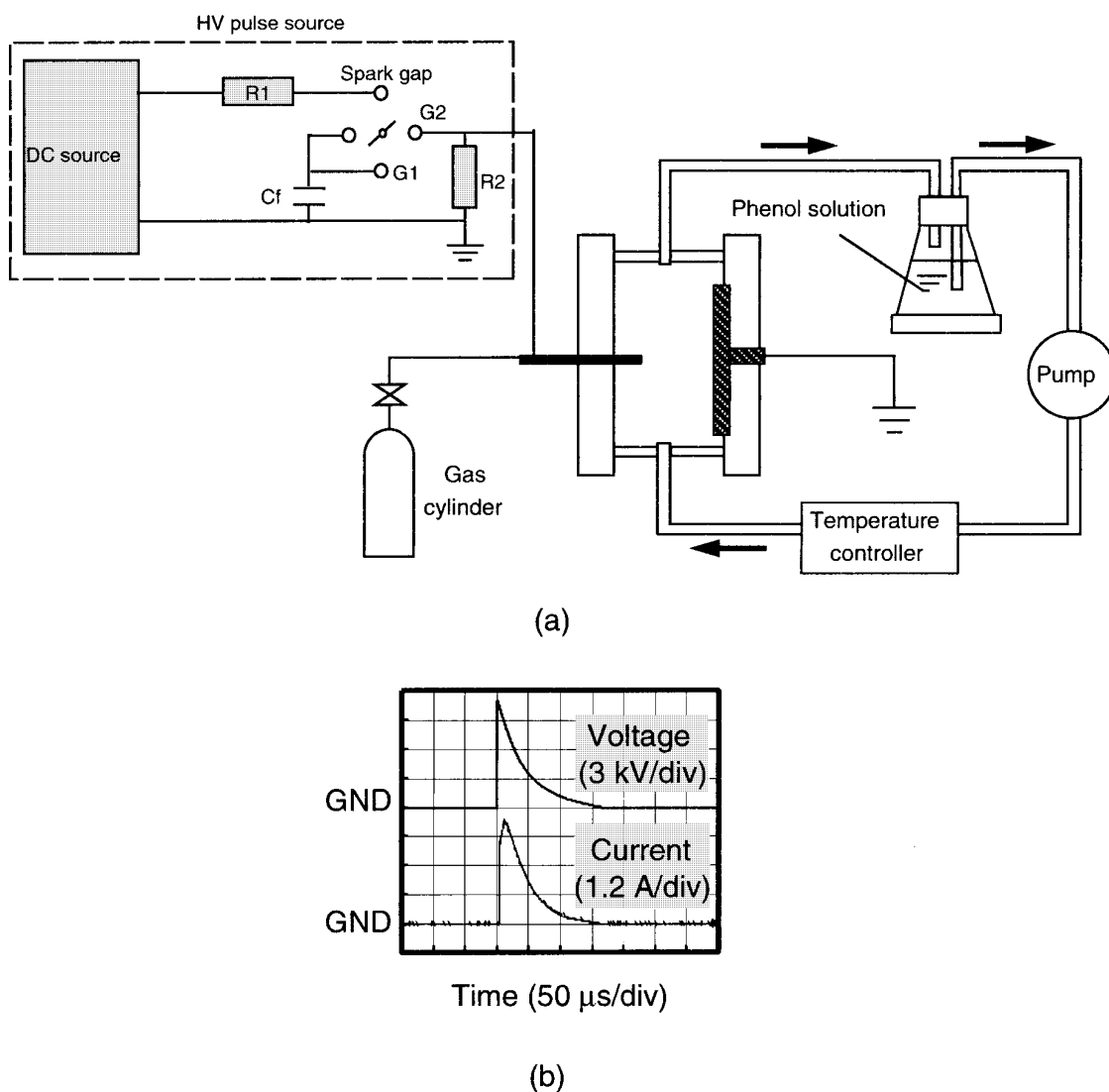
Figure 1. Schematic diagram of the (a) experimental apparatus and (b) an example of waveforms of voltage and current for pulsed-streamer discharge.

investigation, applying fast-rising pulses generates streamer corona discharges, leading to the formation of a non-thermal plasma. Active species (radicals) formed with the pulsed streamer corona discharge can react with the pollutant molecules, converting them to less hazardous or more easily handled compounds. During the destruction of organic molecules by an electron or by a chemical reaction, energy is required to break the chemical bonds. In these systems, the major reactive species involved in the degradation of organic contaminants are the hydroxyl radical, ozone and hydrogen peroxide. Hydroxyl radicals directly attack organic compounds leading to the oxidation of these compounds. Ozone can react directly with organic compounds, or decompose into other radicals which react with the organic compounds. Hydrogen peroxide is important in organic contaminant degradation because in the presence of iron it produces large numbers of hydroxyl radicals through Fenton's reaction [6].

The hydroxyl radical is a short-lived, extremely potent oxidizing agent that is capable of oxidizing organic

compounds, mainly by hydrogen abstraction. This reaction generates organic radicals, which by the addition of molecular oxygen yield peroxyl radicals. These intermediates initiate thermal (chain) oxidative reactions, with the resulting degradation finally yielding carbon dioxide, water and inorganic salts [18].

Practically, it is important in waste water treatment to ensure that the reduced phenols (organic compounds) are not converted into toxic materials. However, the final byproducts and the reaction mechanisms involved in the destruction of organic compounds by the pulsed discharge have not been sufficiently clarified. Therefore, this method has received more attention in recent years because there is still much to be learned. This paper presents results concerning the use of pulsed-streamer corona for the formation of active species and the removal of organic compounds. The effect of gas injection (bubbling) on organic decomposition was investigated. Most of the intermediates and final byproducts were identified and a preliminary study of the reaction mechanism was conducted.

2. Experimental apparatus and method

The experimental apparatus for the treatment of organic compounds with a pulsed streamer corona discharge is shown in figure 1(a). A point-to-plane geometry electrode system was used with a separation distance of 21 mm. The point electrode was either a stainless steel hypodermic needle or a sharp platinum point and the plane was a 20 mm diameter stainless steel disk. The inner diameter of the reactor was 46 mm and the length was 32 mm. The liquid was circulated with a peristaltic pump during phenol treatment and was cooled through a coiled-pipe heat exchanger at ambient temperature. The liquid circulation rate could be adjusted from 20 to 200 ml min^{-1}. A rotating double spark-gap-switch was used to generate high-voltage pulse. Cf was charged through the gap G1 and then the charge stored in Cf was discharged through the gap G2. The spark-gap-switch was rotating at a constant speed with a variable speed motor. The typical oscillograms of the pulse voltage and current are presented in figure 1(b). The principal parameters of the source are: peak voltage, 0–30 kV adjustable; rise-time, several tens of nanoseconds; repetition-rate of pulse, 0–50 pps adjustable (48 pps through this experiment). The schematic diagram of the light detection set-up for obtaining radical emission spectra was shown in a previous study [9].

The concentration of the phenol and byproducts in the solution was measured by using gas chromatography (GC-8A, Shimadzu) with the column packed with Porapak (type P) or by using high-performance liquid chromatography (LC-9A, UV absorption detector, Shimadzu) with the column packed with polymethacrylate gel (RS pak, DE-613, Shodex-Showa Denko). The liquid chromatography ultraviolet detector was set at a wavelength of 254 nm. The eluting solvent comprised of 70% phosphoric acid aqueous solution (0.01M H_3PO_4) and 30% acetonitrile, and 20 μl was injected for each experimental sample. Carbon dioxide was measured by absorption in barium hydroxide followed by back titration with standardized HCl.
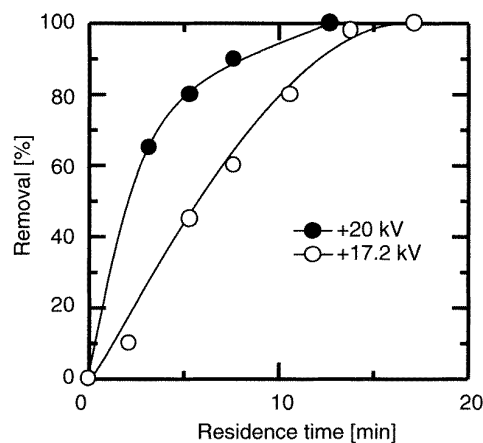
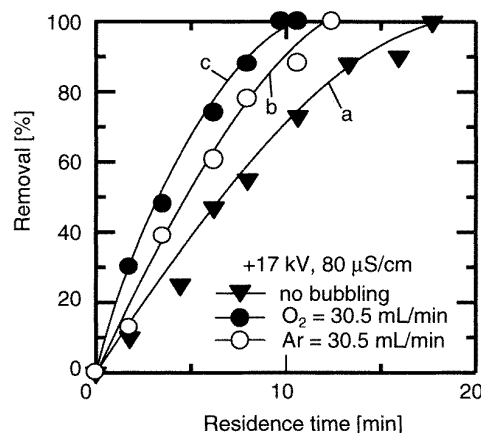## 3. Phenol removal results

3.1. Removal of phenol

3.1.1. Effect of residence time at different peak voltages.
Trace phenol (initial concentration 50 ppm) in aqueous solution was removed by applying pulsed voltage to generate streamer corona discharges in the solution. The conductivity of the solution was 80 μS cm^{-1}. The phenol removal increased with increasing residence time, as shown in figure 2. The open circles are for a peak voltage of +17.2 kV, a liquid circulation rate of 38 ml min^{-1} and a stainless steel needle electrode. The full circles correspond to a peak voltage of +20 kV, a liquid circulation rate of 100 ml min^{-1} and a platinum point electrode. The phenol removal reached 100% after a residence time of about 12.7 min.

3.1.2. Effect of gas bubbling.
In order to investigate the role of different radicals in degrading phenol, oxygen gas and an inert gas (argon) were bubbled separately through the hypodermic needle electrode. Figure 3 shows the

Figure 2. Dependence of phenol removal on residence time for peak-pulse voltages of +17.2 and +20 kV.


Figure 3. Effect of gas bubbling on the phenol removal efficiency at a +17 kV peak-pulse voltage.

experiment results for the removal of phenol by a streamer corona discharge in the solution. Curve a for the case with only a pulsed-streamer corona discharge (no gas bubbling). Curves b and c are for the cases with argon gas and oxygen gas bubbling, respectively. As shown in figure 3, the removal efficiency without gas bubbling reached 100% after about 18 min of treatment. The value of 100% was reached in a shorter time in both cases with gas bubbling than in the case without gas bubbling. With argon gas bubbling, the removal efficiency reached 100% after about 12 min. Furthermore, the removal efficiency with oxygen gas bubbling was the highest, reaching 100% after about 10.6 min.

3.2. Active species formed during oxygen gas bubbling

It is now well known that the hydroxyl radical plays a crucial role in the removal of pollutants from aqueous solutions. But are other radicals besides OH, O and H formed by the discharge, and do they affect the removal? In order to investigate the role of different radicals, first oxygen gas and then argon was bubbled through the hypodermic needle electrode while streamer corona discharges were occurring. Comparing the argon and oxygen results should allow the effect of the OH, O and H radicals to be separated from that of other active species such as ozone, because ozone is formed
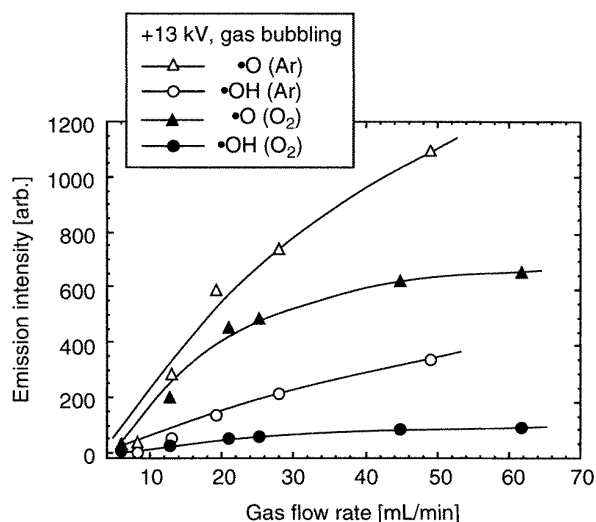
Figure 4. Effect of gas bubbling flow rate on the radical emission intensity at a peak-pulse voltage of +13 kV.

directly by oxygen bubbling [11], but not by argon (inert) bubbling. Figure 4 presents the effect of gas flow rate on the radical emission intensities (radical density) when oxygen and argon gas were bubbled through the discharge. As shown in figure 4, all the radical densities increased when the gas flow rate was raised.

According to the bubble theory of liquid breakdown [10, 11], the physical processes by which radicals are increased during gas bubbling may be for the following: (1) there are more initial bubbles in water near the sharp-point; (2) it is possible to accelerate electrons in the bubbles directly, leading to an increase in the mean-free-path length of the electrons. Therefore higher speed energetic electrons could be obtained so that exciting and ionizing occur in the bubbles and/or water, which make it possible to produce more radicals.

In addition, with argon, the OH and O radical densities were much higher than with oxygen at the same gas flow rates. As known from previous investigations [9], in argon, the hydrogen atom (H radical) emission intensity is clearly the strongest; but in oxygen, the relative intensity of the hydrogen atom is much lower. Using these results, if the OH, O and H radicals were the only radicals that reacted with phenol molecules, then the phenol removal efficiency should be higher with argon gas bubbling than with oxygen gas bubbling, because many more of these radicals were formed with argon bubbling. However, we obtained the opposite result, as shown in figure 3; that is, the removal efficiency was higher with oxygen gas bubbling than with argon gas bubbling. This result indicates that, in the case with oxygen gas bubbling, there are other active species involved with the phenol reaction in addition to the OH, O and H radicals. Most likely, ozone, or superoxide (O_2^-) and singlet oxygen ($^1O_2$), participated in the chemical reactions.

Ozone is formed when oxygen is bubbled into the discharge region. It is known from previous investigations [11] that pulsed-streamer corona discharge with oxygen bubbling into the reactor through the needle electrode produces ozone that, in turn, leads to the decolorization of
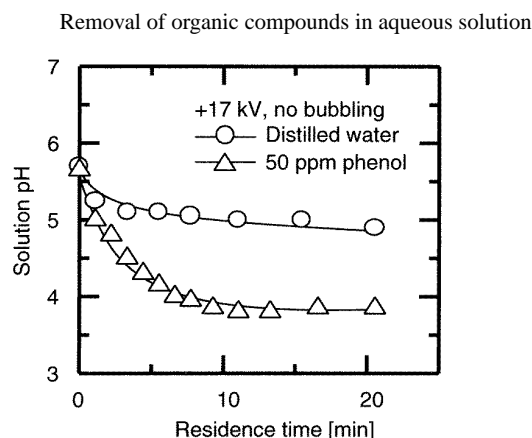
dyes. However, in the case without oxygen bubbling, ozone is not produced, and no decolorization is observed when nitrogen gas is substituted for oxygen. The ozone formed in the discharge region may react with organic compounds. In water, ozone may react directly with dissolved substances, or it may decompose to form secondary oxidants such as OH radicals, which then themselves immediately react with the solutes. These different reaction pathways lead to different products.

4. Byproducts and reaction mechanism

4.1. Variation of the solution pH

In order to investigate product characteristics, the pH of the treated solution was measured. The change in pH with residence time is shown in figure 5 when +17 kV pulsed voltage was applied. With increasing residence time, the pH of the phenol solution decreased rapidly at first, then stopped decreasing after about 8 min. However, the pH of the distilled water stopped decreasing after only about 3 min. For distilled water, the change in pH is due to hydrogen peroxide production during treatment, which results in the solution becoming more acidic. In the case of the treated phenol solution, in addition to hydrogen peroxide, other substances such as organic acids may be produced.

4.2. Products formed by the pulsed-streamer corona discharge

4.2.1. Analysis with high-performance liquid chromatography. Samples of solutions treated both with and without oxygen bubbling were analysed for phenol, pyrocatechol, hydroquinone, 1,4-benzoquinone and resorcinol by high-performance liquid chromatography. The results were more complex with oxygen bubbling than without oxygen bubbling: more than seven peaks were observed in the voltage only case and more than nine peaks with gas bubbling. The retention times for the medium-height fourth, fifth, sixth and seventh peaks corresponded to those of hydroquinone, 1,4-benzoquinone, pyrocatechol and phenol, respectively. The first, second and third peaks were the final byproducts of the chemical reaction. In addition to these peaks, many smaller peaks and an unidentified peak were also observed.

Figure 5. Variation of the solution pH with residence time at +17 kV peak-pulse voltage.
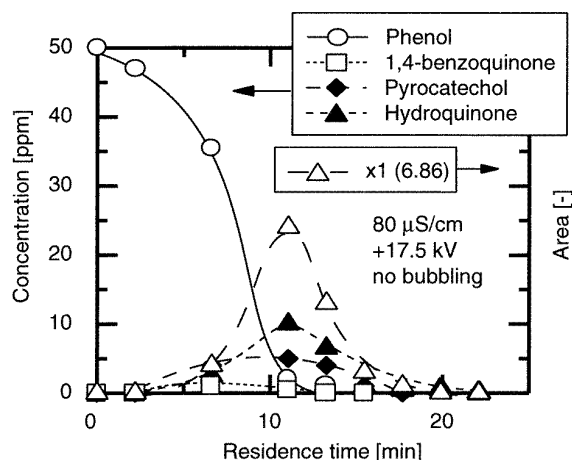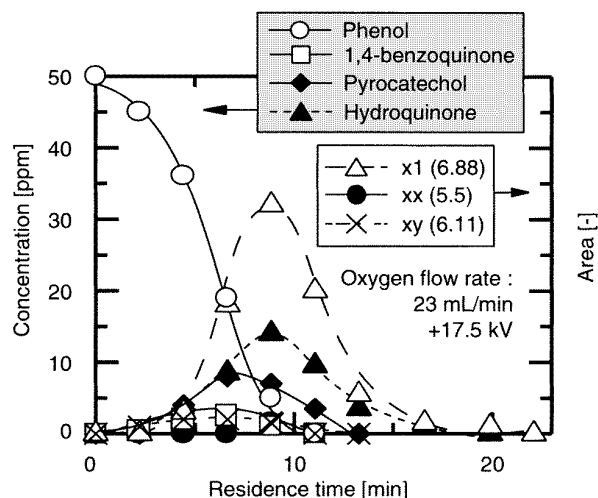
Figure 6. Concentration of byproducts in 50 ppm phenol solution treated with pulsed-streamer corona discharge plotted against the residence time.

These trace intermediate products have not been identified. In the oxygen bubbling case, two extra peaks at retention times of 5.5 and 6.1 min appeared and then disappeared with increasing residence time. When ozone was injected into the reactor (no discharge) to remove phenol, two peaks at 5.5 and 6.1 min were also observed. Therefore the two new peaks are considered to be contributed by the ozone reaction.

The main products produced by the pulsed voltage discharge during the treatment process were hydroquinone, pyrocatechol, 1,4-benzoquinone and other unidentified trace products. These products disappeared when the residence time was increased. Therefore these products are called intermediate products in the treatment process. Figure 6 shows the variation of the concentration of phenol and the intermediate products with increasing residence time. The concentration of 1,4-benzoquinone increased with increasing residence time for the first 6.6 min and then decreased, finally disappearing after 15.5 min. The concentrations of hydroquinone and pyrocatechol begin to increase at a residence time of 2.2 min, kept increasing with residence time up to 11 min and then disappeared after about 22 min and 15.5 min, respectively. To summarize, the phenol and intermediate products were completely removed if the residence time was long enough.

Figure 7 shows the phenol and the intermediate product concentrations as a function of residence time when oxygen gas was bubbled through the discharge. In this case, the phenol and intermediate products disappeared faster, and two new intermediate products (xx and xy) appeared. According to Singer [19, 20], the two new intermediate products may be muconic acid and glyoxal. Again, the phenol and intermediate products were completely removed when the residence time was increased.

However, both with and without oxygen bubbling, final products, the first (Px), second (Py) peaks, and smaller third peak (Pz), remained after treatment. The effect of residence time on the final product concentrations is shown in figure 8. In both cases (with and without oxygen bubbling), before the phenol was completely degraded, final product (Py and Pz) increased as the phenol concentration decreased. After the phenol was completely degraded, the

Figure 7. Concentration of byproducts in 50 ppm phenol processed with oxygen gas bubbling plotted against residence time.
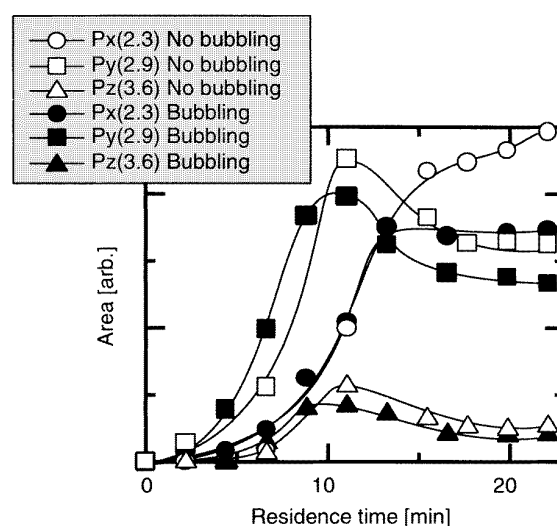
Figure 8. LC peak area of the final products in treated 50 ppm phenol as a function of residence time.

(Py and Pz) concentration decreased slowly. In contrast, final product (Px) slowly increased after the intermediate products disappeared. Here the Px peak was thought to be the hydrogen peroxide, since the retention time of Px was the same as the retention time of hydrogen peroxide; but it was not identified clearly because of the overlapping of other peaks.

The peaks (Py and Pz) slowly changed with longer residence time. This was likely to be due to the effect of the quencher and conductivity. Some anions are well known radical quenchers [6, 13]. This may be explained by the radical quenching effect of the carbonate ions formed. The amount of hydroxyl radicals that are available for reaction with organic compounds, is significantly lower, resulting in a small amount of degradation. In addition, since the conductivity of the solution increases with discharge treatment, higher conductivity will inhibit the formation of streamers and thereby reduces the formation of hydroxyl radicals.

4.2.2. Total carbon and FTIR analysis. In order to investigate the properties of the byproducts formed in the organic compound removal process, total carbon and total organic carbon analyses were performed. The measurement results for various experimental conditions are given in tables 1 and 2. The total organic carbon of the solution treated for 12 min at +20 kV, with 5.0 ml min^{-1} oxygen bubbling decreased by 37% from 50.2 to 31.5 ppm and the total carbon decreased by 31% from 51.6 to 35.6 ppm under the same conditions. In general, the carbon content decreased with increasing residence time. When the solution was treated for 22 min at +17.5 kV, the total carbon decreased by 82.7% without oxygen bubbling, and by 85.8% with oxygen bubbling and the total organic carbon decreased by 83.0% and 86.1%, respectively. Clearly, removal efficiency is higher with oxygen bubbling than without oxygen bubbling. In table 1, phenol was removed after 12 min of discharge treatment, but intermediate products were not removed, therefore only 37.3% of the total organic carbon was reduced. In table 2, both phenol and intermediate products were removed due to longer discharge time, leading to a higher removal percentage. Most of the degraded organic carbon was converted into carbon dioxide, which escaped from the liquid. This was determined by collecting the gas formed by the pulsed-streamer corona discharge and analysing it by absorption in barium hydroxide and by back titration with standardized HCl. Some white sediment was observed, where about 75% of total carbon was converted to carbon dioxide.

As determined from the above results, even after the complete disappearance of the intermediate products, about 10–20% of the total organic carbon remains in solution. In order to identify the final byproducts, Fourier transform infrared spectroscopy (FTIR) analysis was carried out. There was a possibility of a carbon–oxygen double bond and/or open-ring carbon–carbon double bond existing in the treated solution. However, precise results were hard to obtain from only FTIR analysis, as the treated solution was a mixture of several substances. Mass and ultraviolet analysis will have to be carried out in order to identify the final products in detail.

4.3. Reaction mechanisms

4.3.1. Action of the OH radical. It is well known from previous studies that active species such as the OH, O and H radicals, hydrated electron and O_3, are formed from water when high-voltage pulses are applied to generate a streamer-corona discharge in water. The hydroxyl radical reacts with phenol, leading to the formation of hydroquinone, pyrocatechol and resorcinol, with a reaction rate of 4.2×10^9 l mol^{-1} s^{-1} [21]. The reaction mechanism is complex. In the presence of organic compounds, hydroxyl radicals react via a number of pathways, thereby generating reactive organic radicals which undergo further reactions, usually resulting in the oxidation of the organic substrate. The OH radical reacts with phenol to form the dihydroxycyclohexadienyl radical $\cdot C_6H_5(OH)_2$ as follows [5, 22]:

$$C_6H_5OH + \cdot OH \rightarrow \cdot C_6H_5(OH)_2. \tag{1}$$
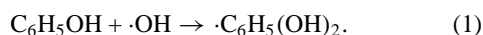
The dihydroxycyclohexadienyl radical $\cdot C_6H_5(OH)_2$ can decay to form the phenoxyl radical $\cdot C_6H_5O$. The phenoxyl radical is an intermediate in the radical formation processes involving phenol and can also be directly formed under the action of ultraviolet light produced by the discharge [23]

$$C_6H_5OH + h\nu \rightarrow \cdot C_6H_5O + e_{aq}^- + H^+. \tag{2}$$
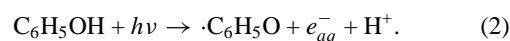
The phenoxyl radical reacts with the OH radical or oxygen to form hydroquinone and pyrocatechol, or other products

$$\cdot OH + \cdot C_6H_5O \rightarrow C_6H_4(OH)_2 \text{ (or products)}. \tag{3}$$
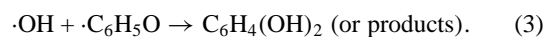
In the presence of oxygen, dihydroxycyclohexadienyl $\cdot C_6H_5(OH)_2$ also reacts easily with oxygen to form the oxygen adduct radical, and the oxygen adduct radical decays in a first-order process to form dihydroxybenzenes [5]

$$\cdot C_6H_5(OH)_2 + O_2 \rightarrow \cdot C_6H_5(OH)_2O_2 \rightarrow C_6H_4(OH)_2 + \cdot HO_2. \tag{4}$$
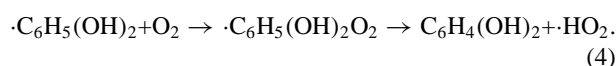
When accumulated in sufficient quantities, dihydroxybenzenes are also attacked by the OH radical to form $\cdot C_6H_4(OH)_3$ which further reacts with oxygen to form trihydroxybenzenes $C_6H_3(OH)_3$.

In addition, the primary oxidation products that are formed are oxidized further to form secondary products such as pyrogallol, 1,4-benzoquinone and 1,2,4-trihydroxybenzene [19, 20]. According to Adams [24], the oxidation of hydroquinone by OH radicals proceeds to form 1,4-benzoquinone.

The intermediate products that are formed are also 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. On the other hand, the intermediate products or organic acids are also oxidized through hydroxylation and hydration, finally forming carbon dioxide [2, 4, 25–27].

4.3.2. Action of the O radical. The reactions of the oxygen atom $O(^3P)$ with organic hydrocarbon play a central role in many important environments. The direct reaction of the oxygen atom with saturated hydrocarbons has been investigated [28, 29]. Direct reaction of the oxygen atom with phenol leads to oxidization of the phenol molecule. In addition, the oxygen atom reacts with water or other molecules to produce the OH radical. The reaction of the oxygen atom with water is

$$\cdot O + H_2O \rightarrow 2 \cdot OH \tag{5}$$

and the oxygen atom reactions with hydrogen peroxide are

$$\cdot O + H_2O_2 \rightarrow \cdot OH + \cdot HO_2 \tag{6}$$

$$\cdot O + H_2O_2 \rightarrow O_2 + H_2O. \tag{7}$$
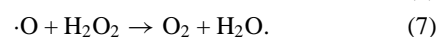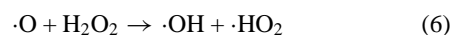
The OH radicals produced by these reactions can further remove organic phenol.

4.3.3. Action of ozone (O_3). Organic contaminants can be oxidized by ozone as well as by intermediates formed from ozone decomposition. Ozone decomposition is complex in water: many transient oxidizing species ($\cdot OH, \cdot HO_2, O^-, O_3^-$, $\cdot O$ and singlet $^1O_2$) are suggested by the literature [1, 16, 30].

Table 1. Degradation characteristics of the phenol solution.

Sample	Conditions	TC		IC	TOC	
		(ppm)	Removal (%)	(ppm)	(ppm)	Removal (%)
1	Control	51.55		1.33	50.22	
2	+20 kV, 12 min, no bubbling	44.81	13.1	3.09	41.72	16.9
3	+20 kV, 12 min, $O_2 = 5.0$ ml min^{-1}	35.55	31.0	4.06	31.49	37.3

Table 2. Degradation characteristics of the phenol solution.

Sample	Conditions	TC		IC	TOC	
		(ppm)	Removal (%)	(ppm)	(ppm)	Removal (%)
1	Control	45.6		0.2	45.4	
2	+17.5 kV, 22 min, no bubbling	7.9	82.7	0.2	7.7	83.0
3	+17.5 kV, 22 min, $O_2 = 23$ ml min^{-1}	6.5	85.75	0.2	6.3	86.1

These species are highly reactive, which may account for the effectiveness of ozone in destroying organic contaminants [16].

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, catechol and hydroquinone, as the major intermediates [30, 31]. On the other hand, 1,3 dipolar cyclo-addition of ozone causes direct ring-cleavage of phenol producing muconic acid or muconaldehyde [19, 20]. These ring-cleavage products have carbon–carbon double bonds and undergo further ozonation yielding organic acids [30, 31]. In addition, ozone reactions can lead to the formation of hydroxyl radicals. These radicals react strongly with a broad range of organic materials [6]. However, it has been proposed that direct oxidation of the phenol molecule by ozone appears to be the dominant reaction in very acidic solutions [20]. Direct oxidation occurs primarily through cleavage of the aromatic ring. Phenol oxidation by radicals arising from ozone decomposition through the intermediates catechol and hydroquinone occurs less frequently in the acidic solutions.

5. Conclusions

The removal characteristics for phenol and its byproducts were studied experimentally by applying pulsed high-voltage to a needle-plate electrode geometry in aqueous solutions. This investigation showed that organic compounds in the solution can be degraded by the resulting streamer-corona discharge. The results obtained in this study led to the following conclusions.

(1) Hazardous organic compounds, such as phenol, were degraded by the streamer corona discharge.
(2) The removal efficiency of hazardous organic compounds increased greatly when oxygen gas or inert gas was injected into the reaction region and was highest with oxygen bubbling.

(3) It has been experimentally verified that, in the case with oxygen gas bubbling, other active species (such as ozone) are involved in the phenol reaction in addition to the OH, O and H radicals.

(4) Reaction byproducts were determined for phenol. The main intermediate products produced with the pulsed-voltage discharge were hydroquinone, pyrocatechol and 1,4-benzoquinone. These intermediate products disappeared when the residence time was increased further.

(5) By analysing the total carbon (TC) of the treated phenol solution, it was found that the total organic carbon (TOC) was reduced by 83% without oxygen bubbling and by 86% with oxygen bubbling. Carbon dioxide emitted in the gas phase was measured by an absorption method. About 75% of total carbon was converted to carbon dioxide.

This investigation has raised many questions that require further study. For example, in addition to the intermediate products of hydroquinone, pyrocatechol and 1,4-benzoquinone, the other intermediate products (xx and xy, etc) and final byproducts need to be identified. The characteristics of the carbon dioxide formed by the reactions also need to be studied in detail.

References

[1] Staehelln J and Holgne J 1985 *Environ. Sci. Technol.* **19** 1206

[2] Nickelson M G, Cooper W J, Kurucz C N and Waite T D 1992 *Environ. Sci. Technol.* **26** 144

[3] Summers R S and Robert P V 1983 Treatment of water by granular activated carbon *Advances in Chemistry 202* ed M J McGuire and I H Stuffet (Washington DC: American Chemical Society) p 503

[4] Carey J H 1992 *Water Poll. Res. J. Canada* **27** 1

[5] Hashimoto S, Miyata T, Washino M and Kawakami W 1979 *Environ. Sci. Technol.* **13** 71

[6] Sharma A K, Locke B R, Arce P and Finney W C 1993 *Hazardous Waste & Hazardous Materials* **10** 209

[7] Willberg D M, Lang P S, Höchemer R H, Kratel A and Hoffmann M R 1996 *Environ. Sci. Technol.* **30** 2526

[8] Sato M, Sun B, Ohshima T and Sagi Y 1997 *Second Int. Symp. Non-Thermal Plasma Technology for Air Pollution Control (Salvador, Brazil, August 11–17, 1997)*

[9] Sun B, Sato M and Clements J S 1997 *J. Electrostatics* **39** 189

[10] Sun B, Sato M, Harano A and Clements J S 1998 *J. Electrostatics* **43** 115

[11] Clements J S, Sato M and Davis R H 1987 *IEEE Trans. Ind. Appl.* **IA-23** 224

[12] Sato M, Ohgiyama T and Clements J S 1996 *IEEE Trans. Ind. Appl.* **32** 106

[13] Joshi A A, Locke B R, Arce P and Finney W C 1995 *J. Hazard. Mater.* **41** 3

[14] Ai-Arainy A A, Jayaram S and Cross J D 1996 *Conference Record of the ICDL 96 12th, Int. Conf. Conduction and Breakdown in Dielectric Liquids (Rome, Italy, July 15–19, 1996)* pp 427–31

[15] Lubucki P, Jayaram S, Cross J D and Al-Arainy A A 1996 *IEEE Annual Report-Conf. Electr. Insul. Dielectr. Phenom (San Francisco, 1996)* pp 730–33

[16] Goheen S C, Mong G M, Pillay G and Camaioni D M 1994 *First Int. Conf. Advanced Oxidation Technology for Water and Air Remediation (London, Ontario, 1994)* pp 83–4

[17] Schuchmann M N, Schuchmann H P and Sonntag C 1995 *J. Phys. Chem.* **99** 9122

[18] Legrini O, Oliveros E and Braun A M 1993 *Chem. Rev.* **93** 671

[19] Singer P C and Gurol M D 1983 *Water Res.* **17** 1163

[20] Gurol M D and Singer P C 1983 *Water Res.* **17** 1171

[21] Halliwell B and Gutteridge J M C 1985 *Free Radicals in Biology and Medicine* (Oxford: Oxford University Press)

[22] Dorfman L M, Taub I A and Buhler R E 1962 *J. Chem. Phys.* **36** 3051

[23] Joschek H I and Miller S I 1966 *J. Am. Chem. Soc.* **88** (14) 3273

[24] Adams G E, Michael B D and Land E J 1966 *Nature* **211** 293

[25] Kokufuta E, Shibasaki T, Sodeyama T and Harada K 1985 *Chem. Lett.* 1569

[26] Joschek H I and Miller S I 1966 *J. Am. Chem. Soc.* **88** (14) 3269

[27] Sharifian H and Kirk D W 1986 *J. Electrochem. Soc.* **133** 921

[28] Andresen P and Luntz A C 1980 *J. Chem. Phys.* **72** 5842

[29] Luntz A C and Andresen P 1980 *J. Chem. Phys.* **72** 5851

[30] Bailey P S 1972 Reactivity of ozone with various organic functional groups important to water purification *Ozone in Water and Wastewater Treatment* ed F L Evans (Ann Arbor, MI: Ann Arbor Science) ch 3

[31] Bailey P S 1978 *Ozonation of Organic Chemistry: Olefinic Compounds* vol 1 (New York: Academic)