Liquid-phase non-thermal plasma technology for degradation of two high strength phenols in aqueous solution

Hsu-Hui Cheng¹*, Shiao-Shing Chen², Yung-Chih Chen³, Yu-Chi Wu², Wei Luen Tseng², Yi-Hui Wang⁴, Min-Pei Ling⁵

¹ Institute of Engineering Technology, National Taipei University of Technology, Taipei, 1, Sec.3, Chung-Hsiao E. Rd., Taipei 10643, Taiwan, R.O.C. (E-mail addresses: dyucina@hotmail.com 886-2-27712171 ext.4123 Fax: 886-2-27214142)
² Institute of Environment Engineering and Management, National Taipei University of Technology, Taipei, 1, Sec.3, Chung-Hsiao E. Rd., Taipei 10643, Taiwan, R.O.C.
³ Institute of Nuclear Energy Research, Atomic Energy Council, Executive Yuan, Wenhua Rd. Jiaan Village, Longtan Township, Taoyuan County, 325 Taiwan, R.O.C.
⁴ Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei, 1, Sec.3, Chung-Hsiao E. Rd., Taipei 10643, Taiwan, R.O.C.
⁵ Department of Health Risk Assessment, China Medical University, Taichung, No.91 Hsueh Shih Road, Taichung, 40402 Taiwan, RO.C.

Abstract

Phenols are toxic to all types of organisms. Elimination of phenols became, therefore, one of the critical and urgent topics in environmental research. In this study, the liquid-phase non-thermal plasma technology was applied as a pretreatment method to treat industrial wastewater containing phenol and catechol. The result of degradation efficiency was higher with the addition of air than that with the addition of argon. More than 99.5% of phenol and catechol were readily removed when the reaction was carried out at the corona discharge after 50 and 30 min, respectively. The degradation of phenol and catechol with pulsed high-voltage discharge was found to follow first order kinetics equation. At G50 value calculated by the equation of energy input, results indicate that the energy efficiency was utilized more in air (phenol: 9.85×10⁻⁷ mol J⁻¹) than that in the argon (phenol: 7.69×10⁻⁷ mol J⁻¹) atmosphere. The intermediates formed in the phenol degradation process are 2-nitrophenol, catechol, benzophenone, propyne, and trace amounts of organic acids products. Besides, the intermediates formed in the catechol degradation process are 1,2-benzedicarboxylic, diphenylmethanone, and some other unidentified products. Phenol and catechol have about 20% and 30% degradation to CO2 and H2O, respectively; indicating 79.5% and 69.5% are converted to intermediates.

Keywords: Liquid-phase non-thermal plasma; organic wastewater; phenol; catechol
1. Introduction

Phenols are toxic to all types of organisms that have been widely used in industry, including oil refineries, dyes, plastics, pharmaceutical, and coke plants (Arutchelvan et al., 2005). Generally, the petroleum refinery, process bleaching of papermaking, and agro-waste water which contain phenol compounds discharged directly without proper pretreatment may cause serious polluted. World Health Organization (WHO) has prescribed a concentration of 1 μg as the guideline for drinking water (WHO, 1996). Elimination of phenols became, therefore, one of the critical and urgent topics in environmental research.

Recently, the considerable attention has been focused on the so-called advanced oxidation processes (AOP) based on the generation of highly reactive species (Hernandez et al., 2002; Lukes et al., 2003). Especially hydroxyl radicals and ozone plays an important role in pollution control system for organic degradation (Carey, 1992). A number of AOPs generate hydroxyl radicals. Ultraviolet photolysis, wet oxidation, and TiO₂ photocatalysis (Sugiarto and Sato, 2001), for example, have all reached the stage of practical applications. However, the hydroxyl radical reactions activated by these methods are clearly slowing (Chen et al., 2002). Compared to its fellow AOP approaches, non-thermal plasma can achieve greater output and more efficiency.

Non-thermal plasma (NTP) produced in water solutions forms the basis of an innovative advanced oxidation technology of water treatment (Sünkä et al., 1999; Lukes et al., 2003). NTP process can remove chemical and biological wastes under the gas, liquid, and solid states. The method can decompose both high- and low-concentration organic wastewater even in a large flux (Hernandez et al., 2002). NTP was produced during the discharge processes where a large amount of high energy electrons and active species (such as active radicals and molecules) are generated for direct oxidation of dissolved organic molecules (Hernandez et al., 2002; Lukes et al., 2003; Chen et al., 2004). However, applying non-thermal plasma technology into organic wastewater cleaning remains scarce and rarely found in previous literature.

In this paper, it got NTP by high voltage power discharged at ordinary air pressure. We selected two phenols of high strength as the represented substance of organic waste to simulate industrial hard decomposed organic wastewater by the liquid-phase NTP in designed gas-electricity mixture water treatment system. The reason of selecting these two phenols is to study the degradation efficiencies as well as their intermediates between one hydroxyl group (phenol) and two hydroxyl groups (catechol) attached on the benzene ring by the NTP process (Amin et al., 2007). On the other hand, as they are relatively stable and soluble in water, their degradation to reach safety levels in the range of 0.1 to 1.0 mg L⁻¹ is not an easy task (Shakir et al., 2008). Hence, this study attempts to design a NTP water treatment system, based on the characteristics of electric and corona discharged in water; the corona discharged reactor has been devised in our lab to degrade organic compounds in wastewater by high voltage power discharged at atmospheric pressure.
In this paper, a water treatment system of gas-electricity mixture high voltage discharge with the addition of gas was used to explore the optimum condition for efficient removal of organic pollutants phenol and catechol by liquid-phase corona discharged in water, and headspace solid-phase microextraction (SPME) combined with gas chromatograph-mass spectrometric (GC/MS) is applied to determine the analysis of phenol and catechol effect after plasma treatment. Therefore, special attentions in this research were given to some important operation parameters affecting the removal efficiency and energy efficiency, including: (1) Comparison of pH and conductivity variation; (2) effects of gas source on degradation of phenol and catechol; (3) kinetics and G<sub>50</sub> yield; (4) variation of TOC and; (5) byproducts and a discussion of the degradation mechanism

2. Materials and methods

2.1 Experimental system

The scheme of experimental set-up is shown in Figure 1. The pulsed power supply is used to provide pulsed energization of the high voltage discharge electrode with peak to peak voltage in the range of 0-30 KV, and the pulsed repetition frequency rate is 70 kHz (EK Series 600W). The pulsed power supply used in this investigation was purchased from Glassman High Voltage, Inc. (High Bridge, NJ, USA). The pulsed output voltage was measured with a high-voltage probe (Tektronix P6015A). The discharge parameters were monitored by a digital oscilloscope (Qmax UM2202).

The needle-plate electrode was placed in the center of a quartz tube (55 mm inner diameter) for generating a corona discharge in water. A stainless-steel hollow needle was used as the discharge electrode. The point electrode of hollow needle, approximately 3.2 cm, is installed in the center of cylindrical reactor on the bottom of the vessel. Only the conical tip of the point electrode was in direct contact with water (Figure 1). Additionally, the stainless-steel round plate with its diameter of 40 mm, used as the ground electrode, is installed at the top of reactor opposite the needle discharge electrode. The distance between the ground electrode and the nozzle can be adjusted. On the other hand, we set the reaction temperamental range from 273 to 323°K, and the air flow rate is controlled in 150 ml min<sup>-1</sup>.

![Figure 1. Schematic diagram of experimental set-up](image-url)
2.2 Chemical analysis

2.2.1 Materials

The headspace solid-phase microextraction (SPME) hold for manual sampling, the polyacrylate (PA-85μm) fiber used in this investigation was purchased from Supelco (Bellefonte, PA, USA). The standards of phenol (purity > 99.5%) and pyrocatechol (purity > 99.0%) were purchased from Merck (Darmstadt, Germany), sodium chloride (purity > 99.8%) was purchased from Nihon Shiyaku Industries, Ltd. (Osaka, Japan). Distilled water was prepared by passing through a Reverse Osmosis/Deionizer System (Hondwen, Luton, USA). Moreover, the standard solutions of two phenols (100 mg L⁻¹) were prepared weekly by diluting the standard solutions with water, and all standards were stored in a refrigerator before using.

2.2.2 GC/MS conditions

All gas chromatographic experiments were performed on an Agilent Technologies 6890N series gas chromatograph, equipped with an Agilent Technologies 5973N mass selective detector (MS) (Agilent Technologies, Wilmington, DE, USA). The helium was used at a flow-rate of 1 ml min⁻¹ as the carrier gas. The injection port temperature was 280 °C. The electron ionization (EI) and the interface temperature were maintained at 230 °C and 280 °C, respectively. The MS was operated on total ion current (TIC) mode, scanning from m/z 45 to 280. For quantitative determination, the MS was operated on the SIM mode. All separations were performed in using an RTX-5MS column (Restek, Ltd. USA), with a 0.25 μm film, 30 m × 0.25 mm. New PA fiber was conditioned in the injection port of a gas chromatograph at 280 °C for 25 min. The used fibers were cleaned by heating at 280 °C for 5 min prior to extraction.

2.2.3 Analytical procedure

The plasma treatment after sample water took 20ml with added the 5.4 g of NaCl, and a magnetic stirring were stirred at a regular speed of 700 rpm in a 50 ml headspace vial. Then the vial was placed on a heat/stir plate. The fiber was introduced through the septum and kept in the headspace of the vial for 20 min at 40 °C. During the extraction, the samples were magnetically stirred at 700 rpm. Subsequently the fiber was with drawn into the SPME syringe needle, which was then pulled out of the sample vial and immediately inserted into the GC injection port for desorption. Desorption was conducted at 280 °C for 25 min. Finally, the target compounds were analyzed under the chromatographic conditions described above. Each sampling was performed in triplicate. Besides, total organic carbon (TOC) of the sample solution was measured using Aurora 1030C TOC Analyzer purchased from O.I. Analytical Corporation in USA.

2.3. Definition of the energy yield value (G₅₀)

In order to compare the discharge energy yield of two phenols under different atmosphere conditions, the value of G₅₀ (mol.J⁻¹) is defined as the molecules number of two phenols converted per
input energy. Here, the yield value was calculated when 50% contaminant was degraded (Grymonpre et al., 2003; Zhang et al., 2007):

\[
G_{50} = \frac{1}{2} \frac{(C - C_0)}{SED_{50}}
\]

where \( C_0 \) is the initial concentration at \( t=0 \) (M), \( C \) is the concentration at \( t \) (min) time, \( SED \) is the specific energy density (Jl\(^{-1}\)), and defined as

\[
SED = \frac{W_{ip}}{\forall} = \frac{1}{2} \varepsilon E^2
\]

where \( W_{ip} \) is input power stored on the pulse-forming capacitor (W), \( \forall \) is solution volume (L), \( \varepsilon \) is permittivity (Fm\(^{-1}\)), \( E \) is electric field (Vm\(^{-1}\)). \( W_{ip} \) was calculated as

\[
W_{ip} = Pt = \frac{1}{2} C_p U^2 f t
\]

where \( P \) is applied power input (W), \( t \) is treatment time (sec), \( C_p \) is capacitance of pulse-forming capacitor (F), \( U \) is charging voltage (V), \( f \) is pulse repetition rate (Hz). The applied power input can be calculated from the following:

\[
P = IV = (IR)I = I^2 R = V \frac{V}{R} = \frac{V^2}{R}
\]

where \( I \) is current (A), \( V \) is voltage (V), \( R \) is resistance (Ω).

3. Results and discussion

3.1. Comparison of the pH and conductivity variation

In the initial experimental condition, the initial phenol and catechol concentration, pH value, electrode distance and gas flow rate were 100 mg L\(^{-1}\), 5.7, 1 cm, 150 ml min\(^{-1}\), respectively. In the presence of phenol and catechol, the pH value of the solution dropped rapidly with the evolution time in 10 min and then remained steady (Figure 2). For this reason, some organic acids were formed. With a further increase of treatment time, the pH value of the solution decreases slightly, and the conductivity of solution of the significant increases (Figure 3), which indicates that the organic acids are smoothly degraded to carbon dioxide. It may be attributed to the following reasons: the oxidative ability of the oxygen-containing radical is fairly strong under acidic conditions (OH\(^- + H^+ + e^- \rightarrow H_2O \)). Consequently, the degradation proceeded rapidly in acidic conditions. Additionally, Sun et al. reported similar findings that the oxidative ability of plasma tends to be stronger in acidic conditions (Sun et al., 1997), and the gliding arc discharge would produce stronger UV radiation when the solution is alkaline. Since ozone is generated during the plasma process, the UV radiation can enhance the degradation of organic compounds by O\(_3\) and the formation of OH\(^-\) accords with the following reactions.

\[
O_2 + O^- + \rightarrow O_3
\]

\[
O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2
\]
\[ \text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}^- \] \hspace{1cm} (3)
\[ 2\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow 2\text{OH}^- + 3\text{O}_2 \] \hspace{1cm} (4)

Figure 2. Variation of pH with treatment time on degradation of phenol and catechol (solution temperature, 323 °K; applied voltage, 9 kV; current, 6 mA).

Figure 3. Variation of conductivity with treatment time on degradation of phenol and catechol under different atmosphere conditions

3.2. Effect of gas source on degradation of phenol and catechol

The effect of additive gas varieties on degradation efficiency is shown in Figure 4. The experimental condition is 100 mg L\(^{-1}\) solution concentration, solution initial pH 5.7, and 150 ml min\(^{-1}\) additive air and argon. The results obtained from measurement of phenol after 50 min to achieve 100% removal for the corona discharge, and catechol after 30 min treatment time to achieve 100% removal for the corona discharge, respectively (gas source: air). Also, the results indicate that the degradation efficiency of phenol and catechol is higher with the addition of air than the addition of argon when other experimental conditions are the same. The reason for the higher degradation efficiency with the
addition of air is that ozone was produced during the discharge process. Meanwhile, ozone in water has the potential to convert free electrons and H into a strong oxidizing species OH radical which then immediately reacts with the two types of phenol. Consequently, the phenol and catechol were almost degraded completely after 50 min and 30 min, respectively. According to previous reports showed that the total amount of the produced ozone had a relation with gas bubbling rate, and there was an optimal gas bubbling rate for ozone production (Ihara et al., 1999). Furthermore, in the liquid-phase corona discharge case, strong ultraviolet light radiates from the discharge channel, leading to the formation of hydroxyl radicals through the decomposition of water molecules. These radicals in the plasma channel can oxidize phenol and catechol in the aqueous solution.

![Graph showing the effect of gas varieties on degradation of phenol and catechol](image)

**Figure 4. Effect of gas varieties on degradation of phenol and catechol**

### 3.3 Kinetics and energy yield value \((G_{50})\)

In a high voltage discharge system, the energy yield was an important parameter to describe the relationship between energy and removal efficiency. The energy yield value \((G_{50})\) has been determined as the number of moles of two phenols removed from the solution by energy of 1J supplied to system \((\text{mol J}^{-1})\). Also, the kinetics can prove energy yield value by the positive correlation between the relative reaction rate constants \((k)\) and energy yields \((G_{50})\) in the gas-electricity mixture discharge process. The degradation of phenol and catechol was found to follow first order kinetics equation. Figure 5 shows the result, which expressed in the form of first-order plots, for the removal of the phenol and catechol in the gas-electricity mixture reactor under air and argon atmospheres, respectively. The first-order kinetics equation is expressed as follows:

\[
\ln \frac{C}{C_0} = -k_1 t
\]

where \(C_0\), \(C\), \(k_1\), and \(t\) are the concentration of two phenols at a given reaction time, the initial concentration, the rate constant \((\text{s}^{-1})\), and reaction time \((\text{s})\), respectively.

The rate constants and energy yields of the degradation of different organic compounds (phenol, catechol and 4-CP) in different operation condition were compared with some other batch reactors, as
listed in Table 1. From Table 1 and Figure 5, the rate constants of phenol and catechol under air condition were higher than that under argon condition. Besides, the catechol has the faster removal rate than that phenol under the air atmosphere (Figure 5). Also, the results indicated that the degradation efficiency of catechol has faster removal rate than that phenol under argon atmosphere, which has the same result mentioned above. In addition, the energy efficiency results can be obtained from calculating the value of $G_{50}$. The $S_{ED50}$ pulse energy form pulse-forming capacitance was 540 J l$^{-1}$ in the reactor (applied voltage: 9 kV). The phenol ($9.85 \times 10^{-7}$ mol J$^{-1}$) and catechol ($7.69 \times 10^{-7}$ mol J$^{-1}$) had the highest energy yield of removal in the case of using air. The argon atmosphere also gave the highest energy yield for the catechol ($8.42 \times 10^{-7}$ mol J$^{-1}$), the higher removal of contaminant. These results indicated that energy efficiency was utilized more in air than that in the argon atmosphere. Additionally, according to previous reported similar findings that the energy yield ($G_{50}$) increased with decreased compounds concentration, the rate constants ($k$) was also increased with higher degradation efficiency of compounds. This was consistent with the findings of the other results reported. Besides, the applied voltage found in the present study was lower than the applied voltage by other results reported. It was found that the energy yield with different conditions (such as discharged types, gas source, treated compounds and reactors etc.) will be changed from the values of $G_{50}$ measured by other studies.

![Graphs showing degradation of two phenols under air and argon atmosphere](image)

**Fig. 5. Degradation of two phenols under air and argon atmosphere**

Table 1. Pseudo-first-order rate constants ($K$) and energy yields ($G$) of the degradation of two phenols under air and argon atmosphere.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gas</th>
<th>$V$ (kV)</th>
<th>$S_{ED50}$ (J l$^{-1}$)</th>
<th>$k$ value (min$^{-1}$)</th>
<th>$G_{50}$ (mol J$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>Air</td>
<td>9</td>
<td>540</td>
<td>$6.83 \times 10^{-2}$</td>
<td>$9.85 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>9</td>
<td>540</td>
<td>$2.77 \times 10^{-2}$</td>
<td>$7.69 \times 10^{-7}$</td>
</tr>
<tr>
<td>Catechol</td>
<td>Air</td>
<td>9</td>
<td>540</td>
<td>$2.38 \times 10^{-1}$</td>
<td>$8.42 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>9</td>
<td>540</td>
<td>$1.50 \times 10^{-1}$</td>
<td>$8.40 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

### 3.4 Variation of TOC

Figure 6 shows the comparison of decrease of total organic carbon (TOC) under different atmosphere and contaminant conditions. In general, the TOC decrease with increasing treatment time,
which indicates that the degraded organic carbon can be converted into CO$_2$, especially to form the aqueous solution (Chen et al., 2004; Zhang et al., 2005). From Figure 6(a), the solution of phenol and catechol that were treated for 60 min and 40 min in gas-electricity mixture water treatment system decreased from 78.45 to 62.84 mg L$^{-1}$ and 66.23 to 46.52 mg L$^{-1}$, respectively, which have about 20% and 30% converted to CO$_2$ and H$_2$O, respectively. And Figure 6(b) indicated that the decrease of TOC under argon atmosphere has the same result mentioned above. Besides, since the initial TOC under air and argon atmosphere were 78.45mg/L (phenol) and 66.23 mg/L (catechol) as shown in the dashed line, the difference between initial and final TOC was the carbon converted to the gas phase. Final phenol and catechol were converted to TOC and shown as “phenol as TOC” and “catechol as TOC” in Figure 6. Consequently, the two phenols are at least degraded into less hazardous hydrocarbons that are easier to remediate with a secondary treatment of completely.

![Figure 6. Decrease of TOC with treatment time under different gas conditions](image)

3.5 Byproducts and a discussion of the degradation mechanism

3.5.1 Analysis of byproducts formation for phenol degradation

The final solutions are analyzed by GC-MS. The main byproducts are 2-nitrophenol, catechol, benzoquinone, and propyne, with trace amounts of organic acids products. The degradations of phenol in gas-electricity mixture reactor under air and argon atmospheres are summarized in the Figure 7. According to this result and the mechanism of phenol oxidation studied in the literature, primary reaction of phenol decomposition is hydroxyl radical attack on aromatic ring; therefore, results showed that the phenol is firstly oxidized to 2-nitrophenol and 1,2-dihydroxybenzene subsequently to quinones (nitrohydroquinone, 2-nitroxy-1,4-benzoquinone) (Li et al., 2007). The primary oxidation products are oxidized further to form secondary products. Opening of the aromatic ring leads to formation of lower molecular weight compounds, mainly organic acids (carboxylic acid groups) (Lukes and Locke, 2005). Finally, carboxylic acids are also mineralized to CO$_2$ and H$_2$O.
3.5.2 Analysis of byproducts formation for catechol degradation

On the other hand, 1,2-benzenedicarboxylic and diphenylmethanone, with trace amounts of organic acids, were primary products of catechol degradation by GC/MS analysis. Figure 8 shows the catechol degradation pathway scheme by liquid-phase non-thermal plasma. The main reactions of hydroxyl radicals with catechol are added to the various ring positions, whereby three different types of trihydroxycyclohexadienyl radicals are formed (Kubesch et al., 2005; Yan et al., 2005). And then continue to yield ring-cleavage products (i.e. diphenylmethanone and carboxylic acid groups). Finally, carboxylic acids are also oxidized to CO₂.

4. Conclusions

The two types of high strength phenol degradation were studied experimentally by the liquid-phase non-thermal plasma in designed gas-electricity mixture water treatment system. In this study, the result of investigation shows that the phenol and catechol existing in the aqueous solutions can be degraded efficiently by the liquid-phase corona discharge. The results to the following conclusions were summarized:

(1) Degradation efficiency was higher with the addition of air than that with the addition of argon.

(2) Degradation efficiency of two phenols was enhanced with the increase of treatment time, thus, more than 99.5% of phenol and catechol were readily removed when the reaction was carried out.
at the corona discharge after 50 and 30 min, respectively.

(3) Gas-electricity mixture water treatment system has been designed to enhance its efficiency for degradation of high strength organic compounds in wastewater. Also, hydroxyl radicals and ozone play important roles in pollution control system for organic degradation.

(4) The intermediates formed in the phenol degradation process are 2-nitrophenol, catechol, benzophenone, propyne, and trace amounts of organic acids products. Besides, the intermediates fromed in the catechol degradation process are 1,2-benzedicarboxylic, diphenlmethanone, and some other unidentified products.

(5) Phenol and catechol have about 20% and 30% degradation to CO2 and H2O, respectively; indicating 79.5% and 69.5% are converted to intermediates.

5. Reference