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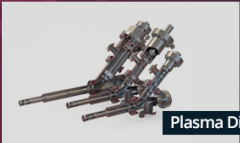
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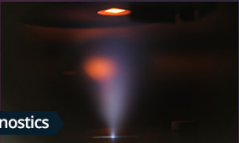
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Oxidative degradation of phenol in aqueous electrolyte induced by plasma from a direct glow discharge

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Abstract

The liquid-phase oxidation of phenol induced by plasma that was generated from direct glow discharges at the tip of a platinum anode in aqueous electrolyte was investigated. Various influencing factors such as the initial pH, the concentration of reactants and the catalytic action of Fe^{2+} were examined. The results suggest that the reaction is a pseudo-first-order kinetic reaction; the initial pH significantly affects the degradation velocity and ferrous ions displayed a remarkable catalytic effect on the oxidation. The major oxidation intermediates were identified with high-performance liquid chromatograph and ion chromatograph analysis. It was found that the degradation proceeded differently in the presence and absence of catalysts and consequently two degradation pathways were proposed.

1. Introduction

With the rapid increase in the number of chemical industries, a huge quantity of wastewater is produced, which causes pollution and degrades the environment. Many of these industrial wastewaters, especially wastewater containing phenolic compounds, are well known to be characterized by high salinity, high acidity, high chemical oxygen demand (COD) and low biodegradability, which means that the effluent cannot be treated by the conventional process [1]. An alternate method of treating such wastewater is by advanced oxidation processes (AOPs), where highly reactive free radicals, especially hydroxyl radicals, are mostly utilized to destroy the pollutants in the water. These processes involve the following main subprocesses: direct ozonization, wet air oxidation (WAO), hydrogen peroxide oxidation, UV photolysis etc. These processes are very effective in degrading the contaminants, but they are not economical [2]: direct ozonation and wet air oxidation are energy consuming, hydrogen peroxide oxidation is costly and UV photolysis is not very efficient. Therefore, it is mandatory to develop efficient

and cheap processes for converting these aqueous pollutants into harmless products [3].

Recently, plasma technology applied to wastewater treatment has attracted a great deal of attention from environmental chemists, mainly because of its amenability to automation, its high efficiency and environmental compatibility. Many processes have been developed, among which the anodic contact glow discharge electrolysis was regarded as the most promising technology because it did not need a special power source or an evacuating system [4]. Using a thin wire anode in contact with the surface of the electrolytic solution, we can observe the formation of a sheath of vapour around the electrode through which the current flows as a glow discharge if the applied voltage is sufficiently high (>420 V). This phenomenon [5] was called 'contact glow discharge electrolysis' (CGDE). In a full CGDE, various active species were produced, including $\text{HO}^\cdot$, $\text{HO}_2^\cdot$, H_2O^+ and O_2^- etc. These highly reactive species could be introduced into the solution by diffusion and steep potential gradients to oxidize the pollutants in the bulk water [6]. Earlier studies have shown that most contaminants can be degraded by means of CGDE [7–13], but there are some practical disadvantages: for example, the discharges cannot be easily controlled, since they are strongly

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dependent on the depth of immersion of the anode [14], and also the electrode is not stable. Based on the principles of the CGDE, we designed a new type of reactor (in which a glow discharge at low voltage applied in the bulk of the electrolytic solution was achieved) and used phenol as a model pollutant. We investigated its degradation behaviour, in the context of wastewater treatment and focusing on the mechanistic and kinetic aspects. To the best of our knowledge, this kind of reactor for wastewater treatment has not been much studied [15–20]. A detailed description of the reactor will be given in the experimental and discussion sections.

2. Experimental

The experimental apparatus consists of a high voltage power supply and a reactor. The reactor vessel contains a needle-to-plate electrode geometry system as shown in figure 1. A pointed platinum anode with a diameter of 0.5 mm sealed into a glass tube was placed at the bottom of a Plexiglas cylinder (inner diameter = 95 mm, length = 250 mm) to generate a glow discharge in water. The cathode was a graphite plate (diameter: 70 mm) suspended above the anode at a distance of about 20 mm. The power supply was a DH 1722-6 dc power unit providing voltages of 0–1000 V and a current of 0–0.3 A. In this experiment, the voltage ranged from 400 to 700 V. The discharge reactor was coated with an outer water jacket to keep the solution at a constant temperature. During the discharge, certain amounts of the solution were periodically sampled from the sampling port for high-performance liquid chromatograph (HPLC) and ion chromatograph (IC) analysis.

The analysis of phenol and its oxidation products were carried out with a HPLC (Shimadzu LC-6A, Japan). The separation and identification of the intermediates was performed using an ODS-18 reversed phase column (Kromail, 250 × 4 mm) at a flow-rate of 1.0 ml min⁻¹ and a column temperature of 25°C. An UV detector was used with a wavelength of 254 nm. The concentration (40–80 mg l⁻¹) of Fe²⁺ and Fe³⁺ ions in the reaction solution were determined spectrophotometrically using a 721-spectrometer with 1,10-phenanthroline as the colour reagent, at a wavelength of 508 nm. The organic acids resulting from the oxidation were identified with IC.

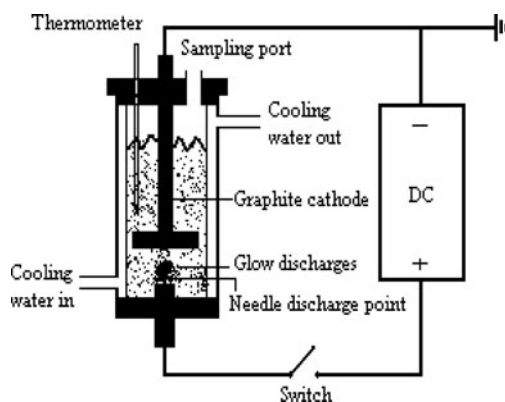


Figure 1. The sketch map of the experimental set-up.

3. Results and discussion

3.1. Voltage versus current characteristics

In order to understand the plasma process completely, a plot of the voltage versus current characteristics are presented in figure 2. A volume of 300 ml of 2 g l⁻¹ Na₂SO₄ was used for the electrolysis.

From figure 2 it can be found that the electrolysis can be divided into three steps. The first step (0–220 V) is the pure electrochemical process. In this step, the current increases with increase in the applied voltage. The reaction includes oxidation and reduction of water: $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$. The second step (200–420 V) is the electrochemical and water vapourization process. The most obvious feature of this process is that the current intensity abruptly decreases with increase in the applied voltage. This phenomenon can be understood if we note that as the voltage increased, an enormous quantity of heat was produced around the anode, vapourizing the water around it. This greatly hinders the flow of current because water vapour is a dielectric. The third step (>420 V) is a complex process mainly including the electrochemical process, vapourization, and gas ionization and pyrogenation. In this process, the water vapour is broken down to give powerful plasmas because of the high potential gradient [5]. When the water vapour is broken down at 420 V, the current intensity becomes smoothly feeble (<540 V) and then abruptly stronger. This phenomenon is a little different from that reported in earlier studies [16, 17]. When the voltage applied is over 500 V, we can observe some sparks near the anode and then it becomes a stable glow discharge when the voltage is over 560 V. From the characteristic plot, we can find that although the experimental set-up is quite different from that of contact glow discharge electrolysis, the mechanism of producing the plasmas is almost the same [17].

3.2. The stability of the anode and optimum degradation voltage

Earlier studies have demonstrated that 500 V was the optimum degradation voltage [10] in the contact glow discharge electrolysis because the platinum anode would melt when the voltage was over 500 V. But in this experimental set-up, no

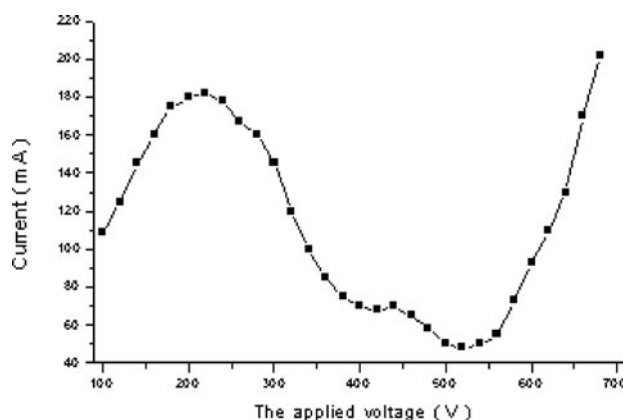


Figure 2. Current versus voltage characteristics ([Na₂SO₄] = 2 g l⁻¹, volume of the electrolyte is 300 mL).

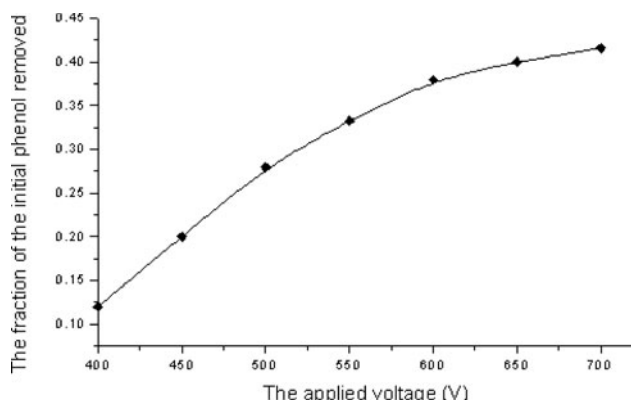


Figure 3. The influence of the applied voltage on phenol removal ($[\text{Na}_2\text{SO}_4] = 2 \text{ g l}^{-1}$, discharge time = 30 min, $[\text{phenol}]_0 = 100 \text{ mg l}^{-1}$).

electrode corrosion or melting was observed even though the voltage was increased to 800 V. This phenomenon proved that this set-up greatly expands the range of the applied voltage. In order to find an optimum degradation voltage within this range, a 300 ml solution containing $2 \text{ g l}^{-1} \text{ Na}_2\text{SO}_4$ and 100 mg l^{-1} phenol ($\text{pH} = 5.0$) was used for degradation under different voltages. The removal rates after 30 min of the discharge at different voltages are illustrated in figure 3.

From the curve in figure 3 it can be seen that the higher the voltage applied, the faster the phenol disappears. For example, at 700 V, for which the degradation went the fastest, 41.6% of phenol could be removed within 30 min, whereas at 650 V, 600 V, 550 V and 500 V it was 40%, 38%, 33% and 28% within the same time, respectively. It was also observed that when the voltage was over 600 V, the increase in voltage did not significantly improve the degradation rate. This can be explained by noting that higher voltage results in higher current intensity and consequently a larger number of free radicals, which in turn enhance the number of termination free radicals by reactions with each other [17]. As a result, too high a voltage will not increase the degradation efficiency correspondingly. Therefore, 600 V may be the optimum voltage under the experimental conditions. We can also see that at 400 V the degradation rate is very slow. This is due to the discharge not being fully developed, which in turn proves that CGDE of phenol is highly efficient.

3.3. The pH effects

The pH of wastewater often plays an important role in the treatment process. Here, the initial concentration of phenol was 100 mg l^{-1} and the applied voltage 600 V. The supporting electrolyte is Na_2SO_4 with a concentration of 2.0 g l^{-1} . The initial pH of the reaction solution was adjusted with 0.1 M NaOH and H_2SO_4 to an expected value. Figure 4 shows the effects of the initial pH of the solution on phenol removal. Faster phenol removal rate was achieved for a solution of relatively higher alkalinity or acidity. As we already know, the oxidative ability of plasmas is stronger in acidic conditions (e.g. the oxidative potential of the hydroxyl radical is 2.70 V at pH 3.0 and 2.34 V at pH 9.0).

When the solution was basic, the amount of plasma increased and the charge distribution of the reactant changes,

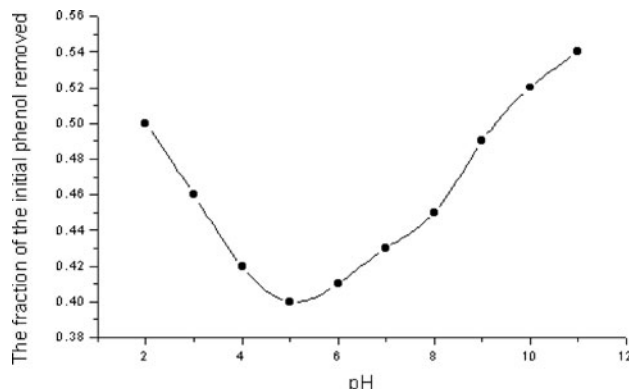


Figure 4. The influence of pH on phenol removal (discharge time: 10 min, $[\text{phenol}]_0 = 100 \text{ mg l}^{-1}$, voltage: 600 V).

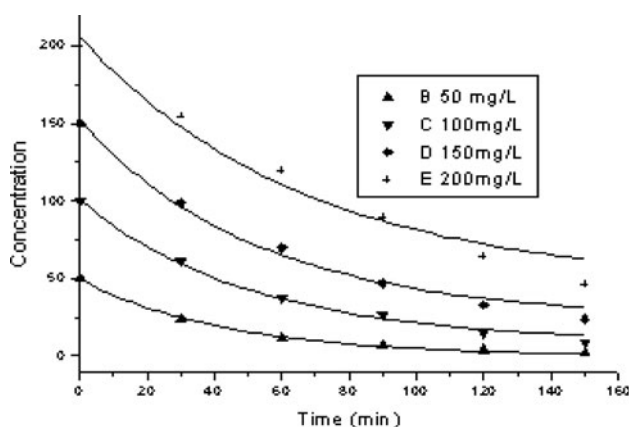


Figure 5. The influence of initial concentration (applied voltage: 600 V, $[\text{Na}_2\text{SO}_4] = 2 \text{ g l}^{-1}$).

which makes it favourable to the attack of the $\cdot\text{OH}$ free radicals [18]. Because most of the wastewater is acidic or basic, the treatment of this kind of water does not need pH adjustment.

3.4. Effect of the initial concentration on phenol degradation

Different initial phenol concentrations (10, 20, 30, 40, 50, 100, 150 and 200 mg l^{-1}) were employed to examine how the initial phenol concentration affected the removal. As shown in figure 5, a higher initial concentration resulted in a larger amount of phenol being removed, but lower relative phenol removal. As the decay curves in figure 5 appeared to be exponential, an attempt was made to apply the data to the integral rate equation for the first-order reaction equation:

$$\ln\left(\frac{c_0}{c}\right) = kt \quad (1)$$

where c_0 , c , k and t denote the initial concentration, the concentration at a given time, the apparent rate constants and the given time, respectively. For each set of data, a straight line with good correlation was obtained, as illustrated in figure 6. The results demonstrated that the reaction for a concentration of 200 mg l^{-1} was a pseudo-first-order reaction and that k decreased with increase in the initial concentration.

3.5. The catalysis of Fe^{2+}

It is well known that some transitional metal ions can catalyse the degradation of an organic substrate in the advanced oxidative processes (AOP), such as those using H_2O_2 , O_2 and ClO_2 , etc as the oxidants. Here, the effect of Fe^{2+} was investigated. In the experiment, the value of pH was maintained at 2.5. The initial concentration of phenol was 100 mg l^{-1} and the volume of the solution was 300 ml. The removal rate of a single substance after 30 min of degradation is exhibited in figure 7.

From figure 7, it can be seen that Fe^{2+} has an evident catalytic effect when its concentration is more than 40 mg l^{-1} , and the removal rate cannot be further enhanced when the concentration of Fe^{2+} is over 80 mg l^{-1} . Therefore, 60 mg l^{-1} is the optimum concentration of the catalyst under experimental conditions, which is similar to the value found by Grymonpre in a pulsed corona reactor [19]. The reason is as follows.

In the absence of Fe^{2+} , the active species in the solution were formed as given below [17]:

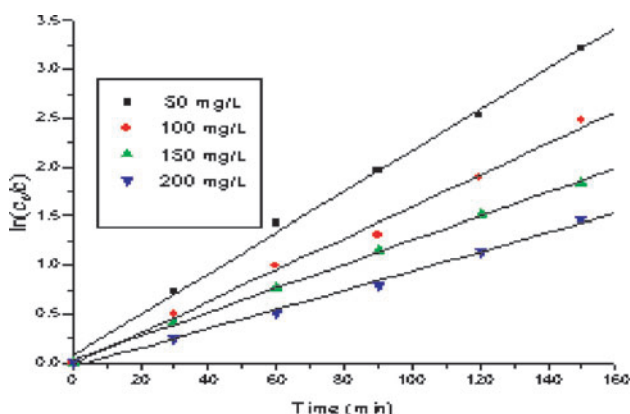
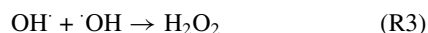
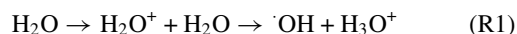


Figure 6. The linear fit of the first-order reaction.

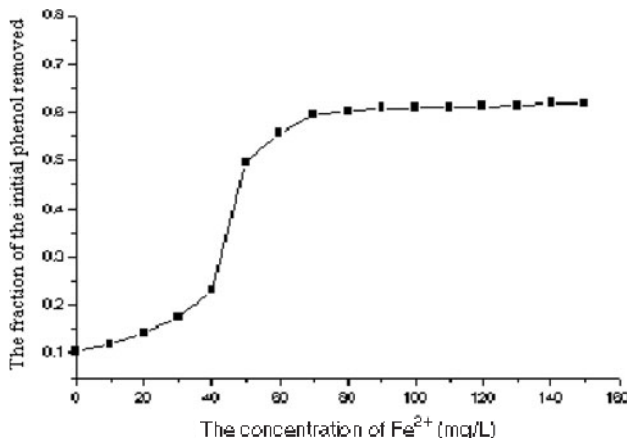
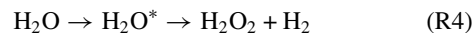
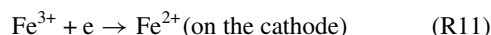
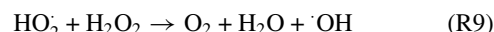
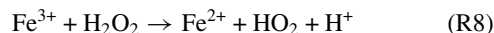
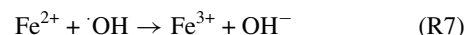
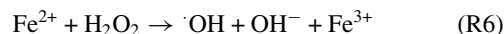


Figure 7. The catalysis of Fe^{2+} ($[\text{Na}_2\text{SO}_4] = 2 \text{ g l}^{-1}$, $[\text{phenol}]_0 = 100 \text{ mg l}^{-1}$, voltage = 600 V).



In the presence of Fe^{2+} , the following process should be added [14]:



It can be seen that in the presence of ferrous ions, more free radicals were produced due to the catalysis of Fe^{2+} , which, in turn, accelerated the reaction.

3.6. Intermediate products and a discussion of the degradation mechanism

In order to obtain the complete profile of the plasma degradation, a series of experiments were carried out to determine the intermediates. First, we investigated the degradation under normal conditions, that is, without any catalyst added. From the experiment it was found that, the results of the degradation were in agreement with that of Tezuka in the CGDE [9]. The major intermediate products included *o*-dihydroxybenzene, hydroxyhydroquinone, *p*-dihydroxybenzene, and carboxylic acids. However, when the reaction was carried out in the presence of Fe^{2+} , benzoquinone

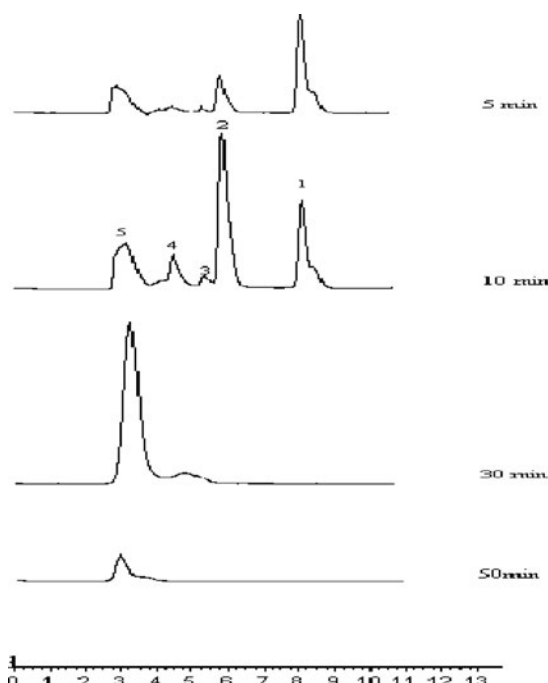


Figure 8. Chromatograph of phenol degradation products in the presence of Fe^{2+} (1: phenol; 2: benzoquinone; 3: *o*-dihydroxybenzene; 4: hydroquinone; 5: organic acids.), mobile phase $\text{CH}_3\text{CN}-\text{H}_2\text{O} = 40 : 60 \text{ (V/V)}$ with addition of $1 : 500 \text{ (V/V)}$ H_3PO_4 .

(not detected in normal CGDE) was detected in considerable amounts besides the intermediate products mentioned above. However, the concentrations of phloroglucin and pyrogallol were very low. So it seems that hydroxyl radicals were not very effective in attacking the benzene rings of the *o*-dihydroxybenzene or *p*-dihydroxybenzene in the presence of Fe^{2+} and this is supported by the supplementary experiment in which *p*-dihydroxybenzene was used as the starting reactant, under the same conditions. Figure 8 shows the plot of HPLC of the reaction mixtures during phenol degradation in the presence of Fe^{2+} .

According to the results of IC analysis the major carboxylic acids (in the presence of Fe^{2+}) were maleic acid, oxalic acid, formic acid and acetic acid.

The HPLC and IC analysis demonstrated that the whole process (in the presence of Fe^{2+}) involves three steps: the first step is the attack of the hydroxyl radical on the aromatic rings of the pollutant, where the predominant products are *o*-dihydroxybenzene, *p*-dihydroxybenzene and *p*-benzoquinone. The second step is the rupture of benzene rings in which the major products are maleic acid, oxalic acid and formic acid. The last step is further oxidation where the above acids were completely decomposed into CO_2 and H_2O .

Based on the analysis above, the degradation pathways were proposed to be as follows.

Under normal plasma conditions [9] it is shown in figure 9. Figure 10 shows the pathway in the presence of catalysts.

Earlier reports have shown that in contact glow discharge electrolysis H_2 is formed in the gaseous phase and H_2O_2

in the aqueous phase [14]. As a result, the concentration of the aqueous hydroxyl radicals is lower. The formation of benzene trihydroxyderivatives is an essential process considering that trihydroxybenzenes are easily oxidized to ring destruction products [20]. Due to the electron-donating character of the phenolic $-\text{OH}$ group and the electrophilicity of the radical [9], the predominant hydroxylation products are *o*-dihydroxybenzene, *p*-dihydroxybenzene, pyrogall and hydroxyhydroquinone. In the presence of Fe^{2+} , hydrogen peroxide was decomposed in considerable amounts to give free hydroxyl radicals due to the catalytic action of Fe^{2+} . It seems that dihydroxybenzenes degrade in two competitive ways in the presence of catalysts. 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 trihydroxyderivatives. It appears that the former is the predominant one [15].

4. Conclusions

From the experiment, the following conclusions can be drawn.

- (i) Increasing the applied voltage and adding the catalyst and some acids and alkalis will be favourable for phenol removal.
- (ii) Phenol can be exhaustively degraded by means of water glow discharges in this set-up.
- (iii) The degradation went differently in the presence and absence of catalysts. In the presence of Fe^{2+} , the major intermediates are benzoquinone, maleic acid, oxalic acid and formic acid.
- (iv) The energy efficiency for decomposition of aqueous phenol in this work was of the order of $10^{-9} \text{ mol J}^{-1}$ at the operating voltage of 600 V, which is comparable with that of pulsed corona discharges in water operating at around 30 kV. It is well known that in a pulsed corona discharge reactor, the operating conditions are very limited: the water must be desalted and the power source must be pulsed, whereas in our process, these procedures did not need to be followed [3–14].

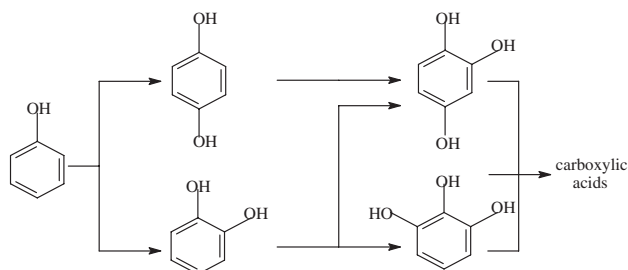


Figure 9. The plasma induced oxidation pathway proposed by Tezuka.

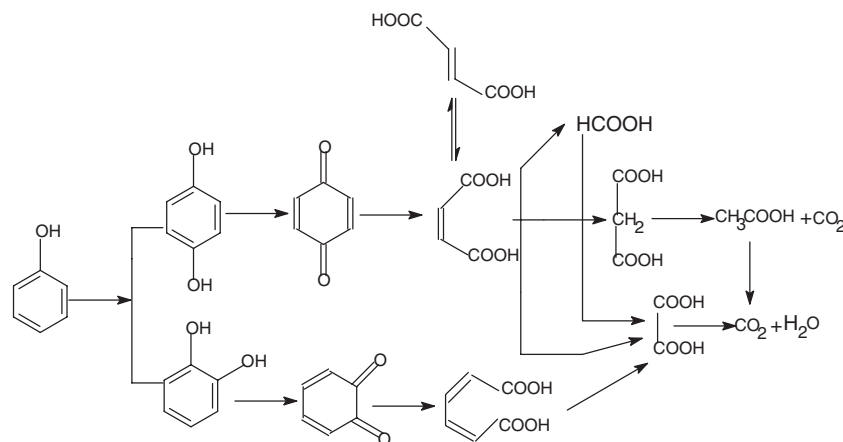


Figure 10. Reaction pathway for phenol oxidation in the presence of Fe^{2+} proposed in this work.

Acknowledgments

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