Degradation of m-dihydroxybenzene by contact glow discharge electrolysis in aqueous

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Abstract. This paper reported the degradation of m-dihydroxybenzene aqueous solution with contact Glow Discharge Electrolysis. The rate of degradation in different conditions such as pH, H2O2, Fe2+, methanol, and other affecting factors were studied. The results showed that there is faster removal rate when the solution is in a relatively higher acidity; H2O2 can improve the efficiency rate. Fe2+ can promote reaction, but radical elimination agent of methanol will decrease the rate of the reaction. On the basis of analyzing the ultraviolet (UV) spectra of the solution and the intermediate products from High Performance Liquid Chromatography-Mass Spectrum (HPLC-MS), reaction pathway was proposed.

1. Introduction
Contact glow discharge electrolysis (CGDE) has been studied since the 1950s [1-3]. CGDE is a novel type of electrochemical process in which plasma was directly produced by the electrical discharge against water. In CGDE, various active species such as hydroxyl radicals, hydrogen peroxide, as well as several other species was generated locally between the platinum wire anode electrode and the surface of liquid solution when the applied voltage was increased to a threshold value, normally 480V. In the reaction zone within the plasma around the anode, vapor H2O molecules were ionized, activated and bombarded each other, and then the free OH radicals were produced through charge transfer, with a resultant of the production of free OH radicals and sometimes H atoms. On the other hand, in the liquid-phase reaction zone near the plasma-anolyte interface, some liquid H2O molecules were broken up into H2, H2O2 and O2 as it is being bombarded by H2O+gas from the anodic plasma. When a mixture of the active species OH, H and H2O+gas diffuse across the primary zone into the bulk electrolyte, they will act as strong oxidizing agents and induce oxidation reaction in the solution. Therefore, CGDE

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could be used to induce some unusual chemical changes in the solution and could be used in an advanced oxidation processes [4-8]. Recently, there have been several reports on the degradation of certain organic target compounds dissolved in water by use of CGDE [9-17]. In this work, degradation of m-dihydroxybenzene aqueous by CGDE has been studied.

2. Experiment
The experimental apparatus consists of a reactor and a high voltage power supply, which is illustrated in figure 1. The reaction vessel is made up of dual glass tubes connected by a sintered quartz glass disk at the bottom. The anode was a platinum wire of 0.5 mm diameter encased in a glass tube located in the bottom center of a glass cylinder reactor, with the needle tip protruding 1 mm from the glass tube. The cathode was a stainless steel stick of 5 cm inserted through the top of the reactor. The power supply was the WYJ-1000V2A direct current power unit which provides voltages of 0-1000 V and current output of 0-2 A. During the reaction course, the cell voltage was adjusted to 480 V and the current was about 80 mA. A glow spot was observed and stretched into the solution of nearly 3mm in height. In addition, the reaction cell was coated by a water jacket, in which the temperature was maintained at room temperature to ensure the long-time reaction.

M-dihydroxybenzene was dissolved in a potassium sulfate solution (2 g·L⁻¹). The pH of the solution was adjusted with dilute sodium hydroxide and dilute sulfuric acid to the expected value. During the reaction, a small portion of the solution was periodically sampled out from the sampling port to measure the reduction of reactant and intermediate product immediately by a UV-V is spectrophotometer (Analytic Jena) and GC-MS and HPLC from Shimadzu Company respectively.

![Figure 1. The schematic diagram of the experimental apparatus.](image-url)
3. Results and discussion

3.1. Accelerated effect of ferrous ions

It is well known that the ferrous ion could react with hydrogen peroxide and produce hydroxyl radicals with powerful oxidizing abilities to degrade organic pollutants. Hickling et al found that the primary yield of oxidizing species was about four times larger than the case without ferrous ion in the solutions [18]. This can be achieved by Fenton’s reaction, therefore, some ferrous sulfate was added into the solution and results were shown in figure 2. The initial concentration of m-dihydroxybenzene was 200 mg·L⁻¹, pH value was 6.00 and applied voltage was 480 V. It can be seen that Fe²⁺ has an evident catalytic effect. Previous studies showed that the predominant products were hydrogen and hydrogen peroxide in the gas-phase and the solution when CGDE was carried out on an aqueous solution without organic substances. Generally, hydrogen peroxide was not able to cause the degradation of pollutants in CGDE. Therefore, the resultant hydroxyl radical from plasma might be responsible for the oxidation of m-dihydroxybenzene as well as its incompletely degraded products. The reasons as follows:

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\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{HO}^\cdot + \text{OH}^- \\
\text{Fe}^{2+} + \text{HO}^\cdot & \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
\text{OH}^- + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{HO}_2^\cdot \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2^\cdot + \text{H}^+ \\
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+}
\end{align*}
\]

From the above reactions, it can be found that in the presence of Fe²⁺, the H₂O₂ produced by the discharge was converted to HO⁻ again. In other word, it accelerates the degradation.

![Figure 2. Effects of ferrous sulfate (U=480 V, T=293 K, c₀=200 ppm, V=200 mL, pH=6.00).](image)
3.2. pH Effects

Special attention was paid to investigate the effects of solution pH on m-dihydroxybenzene degradation since the pH often plays an important role in the wastewater treatment. Figure 3 shows the effects of pH on the degradation of m-dihydroxybenzene. Faster m-dihydroxybenzene removal rate can be achieved in a relatively higher acidity conditions. This maybe presumed that more ·OH was produced in CGDE under acidity conditions.

![Figure 3. Effect of pH on the degradation (U=480 V, T=293 K, c₀=200 ppm, V=200 mL).](image)

3.3. Effects of methanol and hydrogen peroxide

In order to investigate the role of H₂O₂ and methanol in removing of m-dihydroxybenzene, both H₂O₂ and methanol were added into the solution. Here, 100 mg·L⁻¹ H₂O₂ and 100 mg·L⁻¹ methanol were added to 200 mL solutions of m-dihydroxybenzene, respectively, in order to study the degradation

![Figure 4. Effects of methanol and hydrogen peroxide (U=480 V, T=293 K, c₀=200 ppm, V=200 mL, pH=6.00).](image)
behavior. Figure 4 indicates the concentration change of m-dihydroxybenzene in the presence of H$_2$O$_2$ and methanol during 60 minutes of treatment. The results show that the removal efficiency of m-dihydroxybenzene in the presence of hydrogen peroxide is higher than without hydrogen peroxide, and the removal efficiency without hydrogen peroxide and methanol is higher than with methanol. It may be explained that the concentration of ·OH is increased when H$_2$O$_2$ was added into the m-dihydroxybenzene solution and hydroxyl radical is the most responsible oxidant in the degradation of m-dihydroxybenzene.

3.4. Byproducts formation for m-dihydroxybenzene degradation

Special attention was paid to analyze the intermediate in the process of degradation of m-dihydroxybenzene. On the basis of the detailed analysis of the HPLC and HPLC-MS, some intermediate such as benzoquinone, phenol, benzene were produced in the initiation of the discharge. As the electrolysis went on, some carboxylic acids such as formic, oxalic and malonic acids and so on were produced in the process of reaction [19]. All of the intermediate products were easily oxidized continuously under the present conditions. The ultimate products were inorganic carbon, which might exist as bicarbonate or carbon dioxide. Figure 5 gives the variation of intermediate products in degradation process.

![Figure 5. M-dihydroxybenzene degradation pathway in CGDE.](image)

Previous studies have showed that the predominant products were hydrogen and hydrogen peroxide in the gas-phase and the solution respectively, when CGDE was carried out on an aqueous solution without organic substances. Under the experimental condition, the hydrogen peroxide was not able to cause the degradation of m-dihydroxybenzene, therefore, the resultant hydroxyl radical from plasma might be responsible for the oxidation of m-dihydroxybenzene as well as its incompletely degraded products. On the basis of the detailed analysis of the intermediate products and kinetically consideration, it was proposed that the successive attack of hydroxyl radicals on the aromatic rings of starting materials was presumed to be the key steps, especially in the initial stage of overall reactions.
4. Conclusions
From the above experiments, the following conclusions can be drawn:

i) m-dihydroxybenzene can be rapidly, exhaustively degraded by glow discharge electrolysis under water.

ii) The degradation can be greatly accelerated in the presence of Fe²⁺.

iii) Faster m-dihydroxybenzene removal rate can be achieved in a relatively higher acidity conditions.

iv) The degradation can be inhibited in the presence of methanol, and hydrogen peroxide can greatly improve the indole degradation rate.

These wonderful results suggested that glow discharge electrolysis was an efficient method for degradation of m-dihydroxybenzene, and further study is under way.

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