Degradation of 2,4-dichlorophenol by using glow discharge electrolysis

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Abstract

Degradation of 2,4-dichlorophenol (2,4-DCP) in aqueous by glow discharge electrolysis (GDE) has been investigated. Ultraviolet (UV) absorption spectra, atomic force microscopy (AFM), high performance liquid chromatography (HPLC) and gas chromatogram–mass spectrum (GC/MS) are used to monitor the degradation process and to identify the major oxidation intermediate products. It has been found that 2,4-DCP undergoes a series of intermediate step, which leads to form a number of intermediate products, mainly isomeric chlorophenols and aliphatic acids. These products are further oxidized, eventually, mineralized into CO_2 and Cl^-. A degradation pathway for 2,4-DCP is proposed on the basis of detection of intermediate compounds.
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1. Introduction

Chlorinated aromatics, such as chlorophenols, are environmental pollutants of great health concerning. Among the 19 different chlorophenols, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) have been listed by the US EPA as priority pollutants [1]. These compounds have widely been used in the production of pesticides, herbicides, and wood preservatives. They can also be generated as by-product in industrial production, such as the paper pulp bleaching process and water disinfection with chlorine. Being released into the environment, chlorophenols can enter water sources through various transport pathways and can also chemisorb onto soil surfaces and aquatic sediments. Due to their toxicity, they are consequently harmful to human, animal, and fish that are exposed to such contaminated environments. Their conventional destructive technologies include biological treatments, incineration, adsorption over activated carbon, air stripping, etc. Some of these treatments, like the biological treatments, can be affected by the toxicity of some substances; others, like incineration, present considerable emission of other hazardous compounds; and adsorption or air stripping requires a post-treatment to remove the pollutants from the newly contaminated environment [2]. In recent years, advanced oxidation processes (AOPs) have been widely used in wastewater treatment [3–7], the main feature of them is producing •OH radicals to oxidize various organic contaminants. In some sense, the glow discharge electrolysis (GDE) should be considered as one of advanced oxidation processes. Because in the glow discharge process a lot of active species, such as HO• radicals, H• radicals, H_2O_2, and hydrated electrons are generated, which have very high activity [8]. According to the position of both electrodes, two terms, contact glow discharge electrolysis (CGDE) and submersed glow discharge electrolysis (SGDE) [9,10], have been used in literatures. The basic principle is the same. The oxidative potential of the HO• radical is very high potential (2.8 V), only lower than fluorine. Hence, the GDE can provide enough HO• radicals, which made the vast majority of the organic compounds transform into CO_2 and H_2O. Studies on degrading dyes, phenol and naphthylamine using GDE have been reported in our lab [11–13] and the photograph of glow discharges in degradation solution is showed in Fig. 1. In this paper, we report degradation of 2,4-dichlorophenol (2,4-DCP) in aqueous by glow discharge electrolysis.

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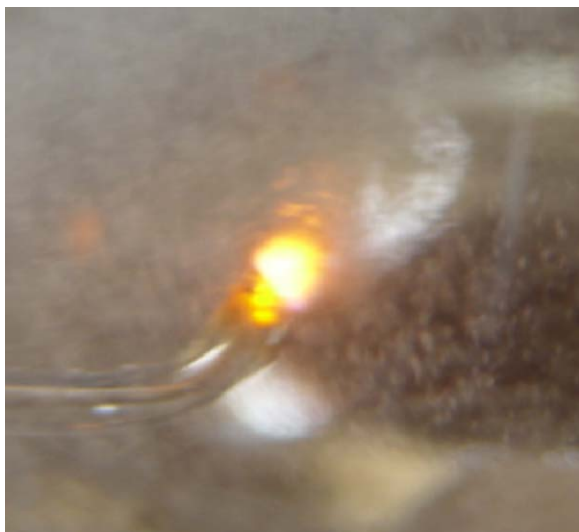*E-mail address:* jzgao@nwnu.edu.cn (J. Gao).

Fig. 1. Photograph of glow discharges in degradation solution.

2. Experimental

2.1. Glow discharge electrolysis reactor and experimental conditions

The experimental apparatus consists of a high voltage power supply and a reactor. The power supply is a DH 1722-6 dc power unit providing voltages of 0–1000 V and a current range of 0–0.3 A. The vessel contained a needle-to-plate electrode geometry system is shown in literature [13]. A pointed platinum anode with a diameter of 0.5 mm is sealed into a glass tube to generate glow discharge in aqueous solution. The cathode is a graphite plate (diameter, 70 mm) suspended above the anode about 10 mm. The discharge reactor is coated with an outer water jacket to keep the solution at constant temperature. There is a magnetic stirring bar at the bottom of reactor to keep the solution mixed well. During the experiments, certain amounts of the solution are periodically sampled from the sampling port for analysis. 2,4-DCP is dissolved in sodium sulfate (2 g/L). The experiments are performed under the conditions as is listed in Table 1 unless otherwise remarked.

Table 1
Experimental conditions

Parameter	Value
Voltage (V)	600
The range of current (mA)	120–150
Distance between electrodes (mm)	10
Diameter of discharge electrode (mm)	0.5
Aqueous Na_2SO_4 (g/L)	2
2,4-DCP (mg/L)	100
Initial pH	6.56
Pressure (kPa)	101.325
Temperature (°C)	25 ± 1
Volume (mL)	250

2.2. Analytical determinations

The ultraviolet (UV) absorption spectra of reaction solutions are recorded by using a model UV-3400 spectrometer (Hitachi, Japan) at intervals.

High performance liquid chromatography (Shimadzu LC-6A, Japan) is used to analyze components of the initial reactant and the different intermediate products in reaction solution. The separation and identification of the intermediates are performed using an ODS-18 reversed phase column (Krosmail, 250×4 mm; flow rate, 1.0 mL/min; mobile phase, $H_2O:CH_3CN$ (50:50) + H_3PO_4 (1‰); wave, 254 nm; pressure, 1.57×10^7 Pa).

The particle size and shape are measured by a Seiko SPI-3800N atomic force microscopy (AFM).

GC/MS analysis is performed on an GC(6890N)/MS(5973N) system (Atrlent, USA) equipped with a DB-5 column (30 m × 0.25 mm ID, 0.25 μm film thickness) (J&W, USA). Electron impact (EI) is used as ionization technique with electron energy 70 eV with m/z range from 20 to 100. Ion source temperature is 230 °C. The injector and detector temperatures are set at 250 °C. Helium serves as carrier gas at a constant flow of 1.2 mL/min (He, 99.999%). After starting under isothermal conditions at 60 °C for 2 min, the temperature is linearly raised at 4 °C/min until 290 °C and then remains the temperature for 30 min. Mass spectral identification of the volatiles is carried out by comparing spectra with those in the NIST02L (National Institute of Standards and Technology, Gaithersburg, MD, USA) mass spectral library and those in the Wiley (New York, NY, USA) mass spectral library.

3. Results and discussions

3.1. UV absorption spectra of 2,4-DCP samples

The degradation process of 2,4-DCP (100 mg/L, 250 mL) is recorded with UV–visible spectrophotometer and the results in the first 90 min are shown in Fig. 2. It is found that there is a rapid decrease of absorption peak at 279 nm, demonstrating the destruction of 2,4-DCP. Lasting for 90 min, approximately, 65% decrease of maximum adsorption peak of 2,4-DCP is achieved.

3.2. Degradation rate

The degradation of 2,4-DCP by GDE is observed to be a function of time. The experimental data on initial oxidation are fitted into the following equation:

$$\ln(A_t/A_0) = kt$$

where A_0 and A_t are concentration of the 2,4-DCP at time 0 and at time t, k the first order rate constant in min^{-1} and t is the time in min. When $\ln(A_t/A_0)$ is plotted against time (Fig. 3) a linear relationship with correlation coefficient $R^2 > 0.9962$ is obtained. The reaction constant k is calculated to be $-0.0162\,min^{-1}$ and the reaction may follow well first order kinetics.
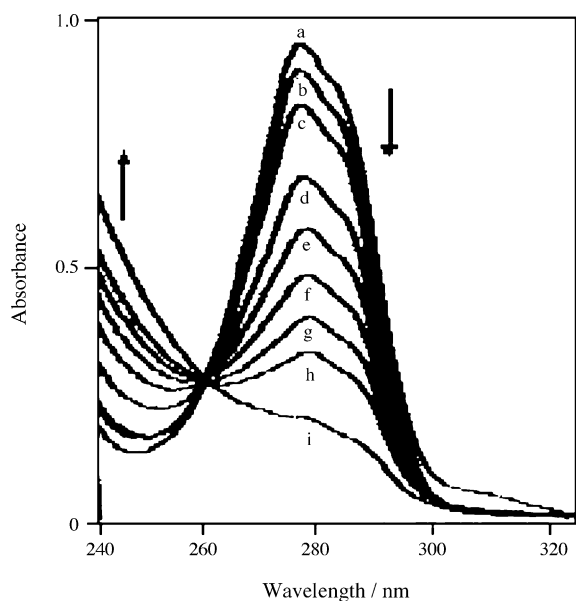
Fig. 2. The UV spectra of 2,4-DCP solution (100 mg/L): (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 40 min, (g) 50 min, (h) 60 min and (i) 90 min.

3.3. pH temporal changes of the degradation solution

The degradation of 2,4-DCP is also followed by in situ measurements of the pH of solution. As observed in Fig. 4, the pH decreases significantly during the first 25 min of GDE, from pH 6.56 ($t = 0$) to pH 3.37 ($t = 25$ min). The reason is that with increasing the reaction time some of lower molecular weight acids are formed. The major intermediate components in the oxidation of 2,4-DCP confirmed by ion chromatography (IC) are organic acids [14,15].

3.4. Atomic force microscopy observations of 2,4-DCP on mica

To examine the physical dimensions of degradation particles, a drop (5 μL) of solution is deposited on a freshly cleaved mica
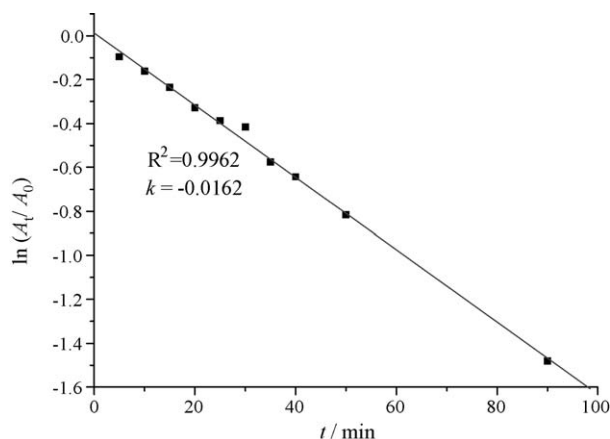

Fig. 3. Relationship between $\ln(A_t/A_0)$ and time during degradation of 2,4-DCP.
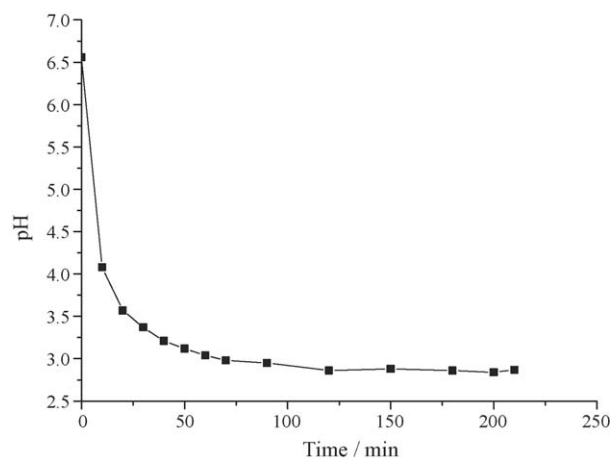

Fig. 4. Change of pH of the solution with time of degradation ($c_0 = 100$ mg/L).

surface and dried under a stream of nitrogen filtered. Atomic force microscopy is done using tapping mode to avoid perturbing the particles. Fig. 5 shows the particles of the 2,4-DCP on the mica surface under different degradation times with different sizes and shapes. There are plenty of 2,4-DCP cluster particles which accumulate on mica surface tightly and make the spacing of particles very little and cause deposit thick because of the high concentration of 2,4-DCP before degradation (a). The cluster particles of molecule weaken clearly after degrading 60 min (b), which illuminate that parts of 2,4-DCP are degraded into small molecule compound. When the solutions are degraded for 120 min, the deposit particles on the mica surface are almost disappeared and inorganic compounds are formed (c). Although it cannot be identified which particle corresponds to which by-product at the present stage, it can be thought from these AFM observations that 2,4-DCP is degraded gradually by glow discharge electrolysis.

3.5. Determination of intermediates by HPLC

HPLC spectra of the degradation solution under the GDE process at various intervals are reported in Fig. 6. Spectrum (a) illustrates the signals of pure 2,4-DCP before degradation. During the time evolution of degradation process (spectra b–d in Fig. 6), a sequence of new signals appear and increase with increasing GDE time. Spectra (b–d) represent the HPLC signals after degradation for 45, 90 and 120 min, respectively. After 45 min of GDE, the signals of 2,4-DCP show a different distribution from spectrum (a). The multiple peaks in spectrum (b) and (c) attributed to the hydroxyl-substituted aromatics, which result from the hydroxyl radical attacking the aromatic ring. Some new signals corresponding to 2-chloro-1,4-benzenediol, hydroquinone, p-chlorophenol and 4,6-dichloro-1,3-benzenediol are observed. Chemical components of degradation solution by GDE are listed in Table 2 within 45 min. After 120 min, 2,4-DCP signals are disappeared, leaving some signal peaks (spectra d in Fig. 6), which can be attributed to form intermediate products. The HPLC finding indicates that the 2,4-DCP is destroyed completely.
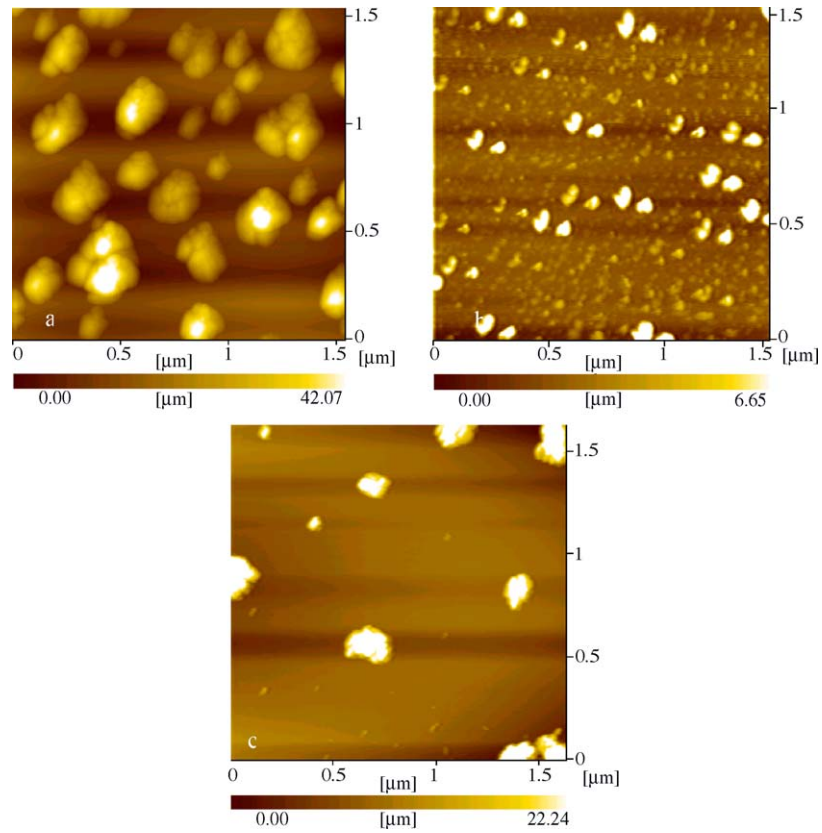
Fig. 5. AFM images of 2,4-DCP (100 mg/L) on mica treated at different degradation time: (a) 0 min, (b) 60 min and (c) 120 min.
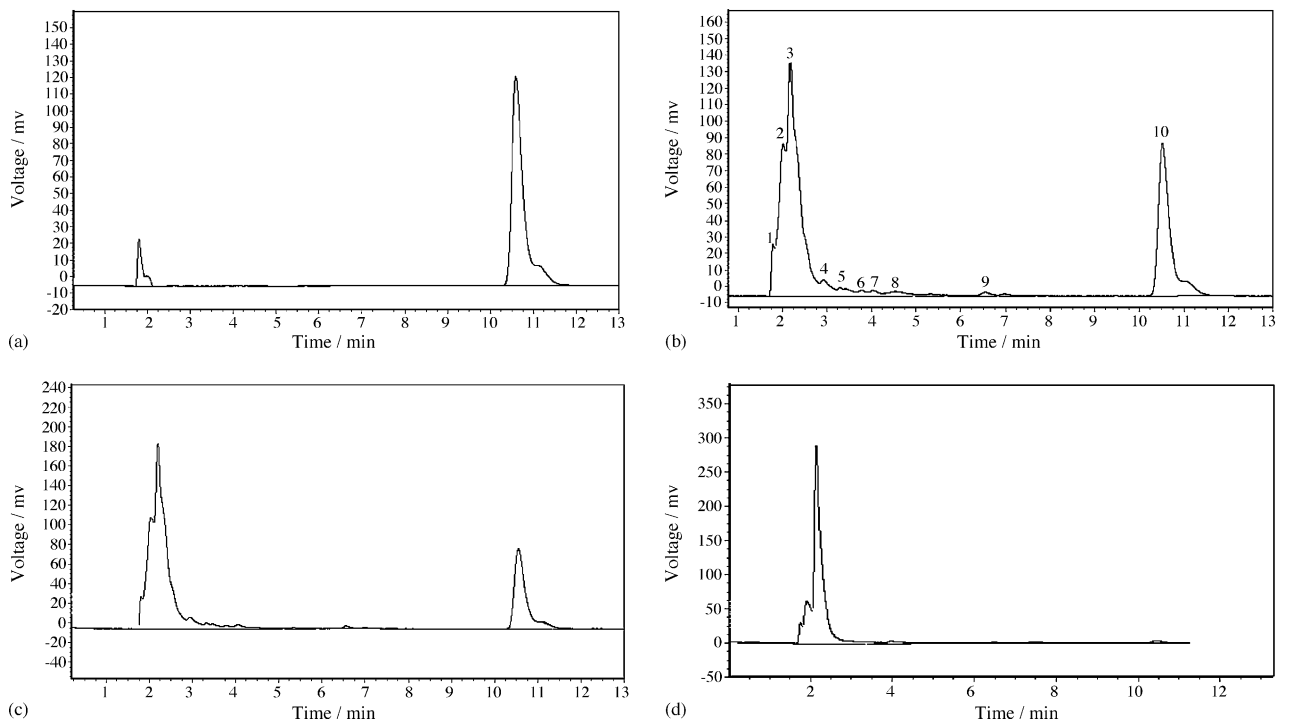

Fig. 6. HPLC spectra changes of 2,4-DCP in GDE reaction at various times: (a) 0 min, (b) 45 min, (c) 90 min and (d) 120 min.

Table 2
Chemical components of degradation solution by GDE in 45 min

Peak no.	Compound name	Molecular formula	Retention time (min)	Content (%)
1	–	–	1.815	2.062
2	–	–	2.057	18.847
3	2-Chloro-1,4-benzenediol	$C_6H_5O_2Cl$	2.215	47.157
4	Hydroquinone	$C_6H_6O_2$	2.948	2.838
5	–	–	3.340	0.712
6	–	–	3.473	0.911
7	p-Chlorophenol	C_6H_5OCl	3.790	0.576
8	–	–	4.065	1.075
9	4,6-Dichloro-1,3-benzenediol	$C_6H_4O_2Cl_2$	6.598	0.469
10	2,4-Dichloro-phenol	$C_6H_4OCl_2$	10.582	23.599

Table 3
Organic compounds detected by liquid–liquid extraction coupled with GC/MS

Peak no.	Compound name	Molecular formula	Molecular weight	Hold time (min)	Content (%)
1	4-Chloro-cyclohexanone	C_6H_9OCl	132	5.741	0.339
2	2,4-Dichloro-phenol	$C_6H_4OCl_2$	162	7.777	48.629
3	p-Chlorophenol	C_6H_5OCl	128	8.371	0.700
4	2,6-Dichloro-phenol	$C_6H_4OCl_2$	162	8.533	0.165
5	Hydroquinone	$C_6H_6O_2$	110	10.575	0.333
6	4,6-Dichloro-1,3-benzenediol	$C_6H_4O_2Cl_2$	178	12.093	1.664
7	2-Chloro-1,4-benzenediol	$C_6H_5O_2Cl$	144	12.404	15.470
8	2,4,6-Trichloro-phenol	$C_6H_3OCl_3$	196	12.856	2.480
9	4,5-Dichloro-1,2-benzenediol	$C_6H_4O_2Cl_2$	178	13.089	1.667
10	3,4-Dichloro-1,2-diol-benzene	$C_6H_4O_2Cl_2$	178	13.728	28.554

3.6. Degradation products of 2,4-DCP analyzed by GC/MS

Formation of intermediates in the degradation process is further confirmed by GC/MS technique. The sample for GC/MS measurement is prepared from the reaction solution which is extracted by ether. The results of GC/MS measurement are displayed in Table 3. The GC/MS of intermediates appear 10 peaks (Fig. 7). It is observed that within 45 min in GDE, several breakdown products of 2,4-DCP form, including 4-chloro-cyclohexanone (1), 2,4-dichlorophenol (2) p-chlorophenol (3), 2,6-dichloro-phenol (4), hydroquinone (5), 4,6-dichloro-1,3-benzenediol (6), 2-chloro-1,4-benzenediol (7), 2,4,6-trichloro-phenol (8), 4,5-dichloro-1,2-benzenediol (9), 3,4-dichloro-benzene-1,2-diol (10). These compounds may be considered as primary degradation products of 2,4-DCP.

The detection of the lowest molecular weight compound has been done by using the ion chromatography [14,15]. Results obtained are summarized aliphatic acids, such as oxalic, formic, fumaric, maleic, malonic, tartaric, and tartronic acids. As has been already pointed out in Fig. 4, the decrease of pH value implies that some organic acids produce during the degradation processes. 2,4-DCP is hydroxylated, producing a lot of small molecules of organic acid after opening the rings and finally mineralize to CO_2 and Cl^-.

3.7. Reaction pathways for 2,4-DCP degradation

On the basis of detailed analysis of intermediate products, it is supposed that the oxidation will start at the aromatic hydroxylation involving hydroxyl radical generated in the solution exposed to the plasma. The attack of hydroxyl radical occurs most favorably at para- and ortho- position, due to the electron-donating behavior of the phenolic OH group and the electrophilicity of the radical. When the benzene rings are broken, the major products
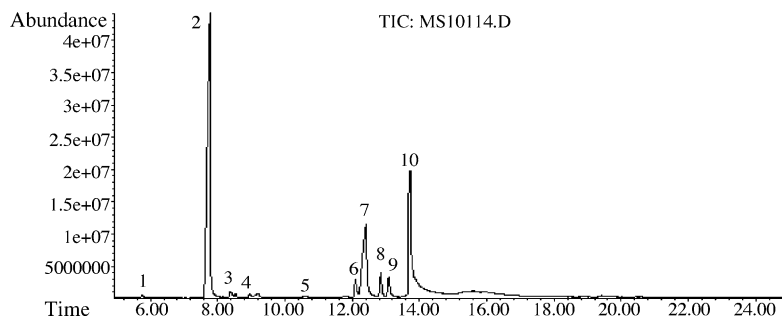

Fig. 7. GC–MS spectroscopy of the main component of the 2,4-DCP of degraded products.
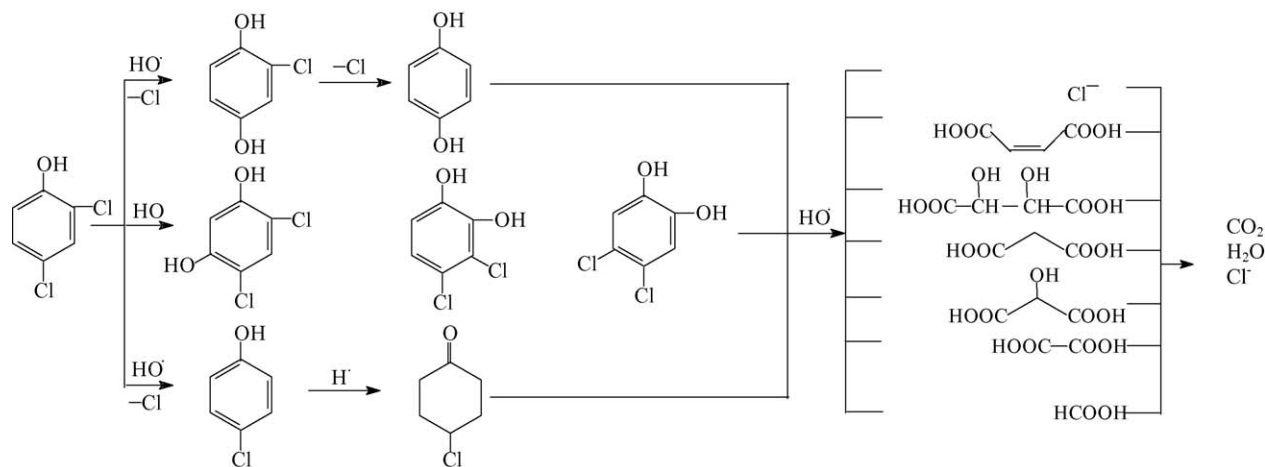
Fig. 8. Proposed reaction pathway for 2,4-DCP by GDE.

are maleic acid, oxlic acid and formic acid, eventually all these acids are completely degraded into CO_2 and H_2O. The pathway can be described as follows (see Fig. 8).

4. Conclusion

The degradation of 2,4-DCP has been examined in aqueous by glow discharge electrolysis. It is found that the hydroxylation of benzene ring is started first, and then some of lower molecular weight organic acids are formed, finally, all of organic compounds are completely mineralized.

Acknowledgements

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