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Removal of 2,4-dichlorophenol as herbicide's by-product by Fenton's reagent combined with an electrochemical system

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ABSTRACT

2,4-dichlorophenol (2,4-DCP), which is known as a by-product from herbicide utilization, is a priority toxic organic pollutant listed by U.S. EPA. The application of electrochemical system combined with Fenton process has been investigated here in order to know the feasibility of continuous electro-regeneration of ferrous ion for enhancement of 2,4-DCP degradation in the Fenton's reagent solution. The operating parameters such as pH, current density, H_2O_2 to Fe^{2+} (H/F) mole ratio and H_2O_2 feeding mode of operation were also investigated to determine the optimum operating condition. From the experimental data, it was found that current density of 0.05 mA/cm^2 with the H_2O_2 to Fe^{2+} (H/F) mole ratio at 30 and operating pH of 3 could completely remove 1 mM 2,4-DCP up to 70%. Improvement in efficiency and stability of process could be achieved by modification of H_2O_2 feeding mode from one-time initial feeding mode to the step feeding mode of operation that could reduce toxicity possibility and mineralization rather than only one-time initial feeding. Additionally initial degradation rate was investigated by the first-order model for using in the process optimization indicator. HPLC and IC data were applied to identify the intermediates occurred among the reaction. For this experiment, 2-chlorophenol, phenol, hydroquinone, p-benzoquinone, maleic, acetic, oxalic, and formic acids were found as the main oxidation intermediates. Moreover, a degradation pathway for 2,4-DCP oxidation was proposed on the basis of intermediate compounds that were detected.

Keywords: 2,4-dichlorophenol(2,4-DCP); Electrochemical system; Fenton process; Hydroxyl radicals; Operating parameters; Feeding mode of operation

1. Introduction

Chlorophenols are widely used chemical products, and also generated by a number of industrial manufacturing processes. Upon entering to environment, they are toxic persistent organic pollutants, causing considerable damage, threat to aquatic ecosystem and human health [1,2]. Their environmental risks are acute toxicity, emission of strong odor, bioaccumulation, resistance to biodegradation, and also suspected mutagens and carcinogens to living things [3]. 2,4-dichlorophenol (2,4-DCP) has been priority chlorinated organic pollutants listed by the U.S. EPA [4]. It is a chemical precursor that contributes principally to the manufacture of a widely used herbicide 2,4-dichlorophenoxy acetic acid (2,4-D). After the herbicides have been applied to agricultural sites,

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2,4-DCP is the major transformation product of 2,4-D by solar photolysis and/or microbial activities in natural water [5,6]. 2,4-DCP has also been found in disinfected water after chlorination, in the flue gas of municipal waste incineration, or in pulp and paper wastewater [7,8]. It has been realized that 2,4-DCP may cause some pathological symptoms and change the endocrine systems of humans [9,10]. The strong resistance to physical, chemical, and biological treatments of chlorophenols causes hazardous effects on living organisms including human beings. The accumulation of chlorinated aromatic compounds in the environment has become a serious problem. Nowadays, it is urgent to develop an effective method to treat these contaminants. Advanced oxidation processes (AOPs) are a possible alternative that can provide the oxidation of refractory and hazardous organic compounds. Fenton process is one of the most powerful AOPs that can be used to oxidize organic matter in water such as phenols, chlorinated phenol and herbicides. This method generates a hydroxyl radical (·OH) from addition of the solution containing hydrogen peroxide (H_2O_2) and iron catalyst known as Fenton's reagent. In Fenton process Fe^{2+} and H_2O_2 are externally applied, whereas in an electrochemical system, ferrous ions can be on-site generated electrochemically [11]. However, most research studies primarily focused on electro-generation of H_2O_2, but electro-regeneration of Fe^{2+} is largely neglected. Here, the application of an electrochemical system combined with Fenton process was investigated in this study using electrical current to induce the reduction of ferric hydroxide sludge to form Fe^{2+}, thus reducing the sludge disposal cost which is one of the major drawbacks of the ordinary Fenton process [12]. In this process, Fe3+ can be directly reduced to Fe^{2+} by an electron supplied from electrical current which is more effective and rapid [13]. This study aims to investigate the performance of 2,4-DCP removal by application of an electrochemical system combined with the Fenton process for continuous electro-regeneration of ferrous ions. The operating conditions that were considered in this study were operating pH, current density, H_2O_2/Fe^{2+} ratio and H_2O_2 feeding mode of operation. Then the optimal operating conditions were selected. The intermediates from 2,4-DCP oxidation were identified and the oxidation pathway was also proposed from this study.

2. Materials and methods

All high purity grade chemicals were purchased from Merck. Synthetic wastewater containing 1 mM of 2,4-DCP was prepared by dissolving 2,4-DCP with de-ionized water (Millipore system with a resistivity of 18.2 MΩ cm^{-1}). The required pH was adjusted by addition of HClO4 or NaOH as necessary. An acrylic reactor of 15 cm × 20 cm × 20 cm with 5 L of working volume was used for experiments on application of the electrochemical system combined with the Fenton process. The electro-Fenton anode nets were made from mesh-type titanium metal coated with IrO_2/RuO_2 and the cathodes were stainless steel nets. All electrodes were connected to the DC power supply, discharged electrical current constantly into the process system. Two mixers were installed to provide complete agitation in the reactor. A calculated amount of catalytic ferrous sulfate was added as the source of Fe^{2+} in this experiment. H_2O_2 was added into the reactor with turn on power supply to start the reaction after. At selected time intervals of 90 min 2,4-DCP, COD, TOC, Fe^{2+}, and H_2O_2 were measured for investigating the effect of operating parameters on the process performance. The samples were immediately injected into tubes containing NaOH solution to stop further reaction and then were filtered through 0.22 μm syringe micro-filters to separate precipitated iron from the solution. 2,4-DCP concentration was determined by high performance liquid chromatograph (HPLC Thermo Scientific Model) equipped with a UV detector (Finnigan Spectra System UV1000). The separation column is a reverse-phase column (Shodex Asahipak, ODP-50 6D 4.6 mm × 250 mm, 5 μm) and a mobile phase consists of acetonitrile : water : acetic acid (69 : 30 : 1). H_2O_2 concentration was measured by a spectrophotometer (Shimadzu UV-1201) at 400 nm wavelength, using $K_2Ti(C_2O_4)_3$ (analytical grade) as an indicator. Ferrous concentration was determined, according to Standard Methods [14] by light absorbance measurement at 510 nm after complex with 1, 10-phenanthroline using a UV-VIS spectrophotometer. According to the Standard Methods [14], closed-reflux titrimetric method was used for COD measurement in after samples were left overnight to remove the residual H_2O_2 that might remain in the sample solutions [14]. TOC was measured by an Elementar-liquid TOC (Germany) analyzer with the high temperature combustion method. High performance liquid chromatography (HPLC) and ion chromatograph (IC) (Dionex DX-120) equipped with RFC-30 EGCII (KOH), IonPac® AG 11 guard column (4 mm × 50 mm), IonPac® AS11 analytical column (4 mm × 250 mm), ASRS®-Ultra II (4 mm) suppressor and conductivity detector were applied to identify the intermediates that might occur during the reaction. All experimental scenarios were duplicated.

3. Results and discussion

3.1. Electrolytic, Fenton and electrochemical combined Fenton's reagents process in 2,4-DCP degradation

Control experiments were carried out to investigate effect of electrical current density on 2,4-DCP degradation. From the results shown in Fig. 1, it was found that the electrochemical system alone with electrical current densities at 0.05 and 0.12 mA/cm^2 could remove 2,4-DCP at low percentage range about 5–8%, while applying Fenton process and electrochemical system combined

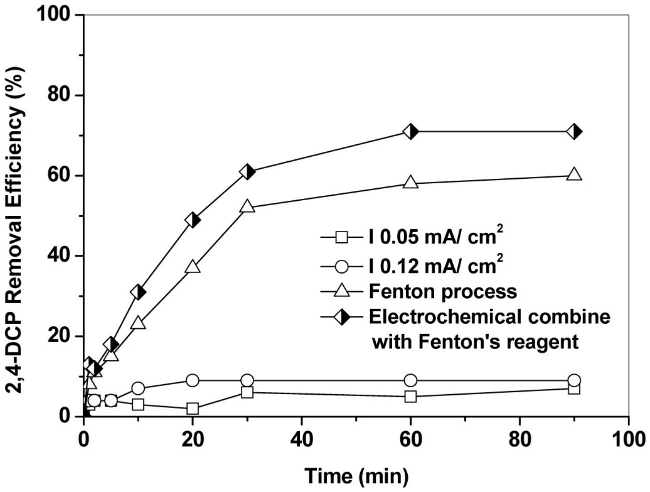

Fig. 1. 2,4-DCP removal efficiency by various processes. ([2,4-DCP] = 1 mM, $[Fe^{2+}]$ = 0.1 mM, $[H_2O_2]$ = 1 mM, pH = 3, current density at 0.05 and 0.12 mA/cm^2.(The electrochemical system combined with the Fenton process used current density of 0.05 mA/cm^2.)

with Fenton's reagents process could remove 2,4-DCP as high as 60% and 70%, respectively. The results indicate that electrical current in the absence of Fenton's reagent obviously could remove 2,4-DCP at a low efficiency level but the removal performance could be enhanced with Fenton process as a result of continuous hydroxyl radical generation that can be confirmed by an increase in the initial degradation rate (0.009 mM/min), compared to the Fenton process without electrical current (0.083 mM/min) as shown in Table 1.

3.2. Effect of operating pH

Operating pH is usually considered to be a significant parameter that can affect Fenton reaction's efficiency. The effective pH was around 2–4 in the conventional Fenton process, depending on the kind of pollutants to be removed. Here, the effect of operating pH for 2,4-DCP removal by the electrochemical system combined with the Fenton process has been investigated. The results obtained from this experiment are shown in Figs. 2a and 2b. From the results obtained here, pH 3 was the best condition for 2,4-DCP removal by the electrochemical system combined with the Fenton process as a result of a higher initial degradation rate than those of other pHs as shown in Table 2. The formation of $(Fe(II)(H_2O))^{2+}$ was expected to occur and reacted with hydrogen peroxide. In addition, the scavenging effect of hydroxyl radicals by hydrogen ions could become significant at a very low pH that might also inhibit the process efficiency. In contrast, at pH above 3.5, the performance of process significantly decreased, mainly due to a decrease in the dissolved fraction of iron species [15,16]. Consequently, less amount of dissolved Fe(II) species could be reacted toward H_2O_2. Then the process performance was affected

Table 1
Initial degradation rate of 2,4-DCP removal by various process ([2,4-DCP] = 1 mM, $[Fe^{2+}]$ = 0.1 mM, $[H_2O_2]$ = 1 mM, pH = 3, electrical current 0.05 mA/cm^2)

Type of process	Removal efficiency (%)	Initial degradation rate (10^{-3} M/min)*
Electrolysis (Current 0.05 mA/cm^2)	7	0.009
Fenton process (No current)	60	0.026
Electrochemical system combined with Fenton process (Current 0.05 mA/cm^2)	71	0.083

* In 20 min of reaction time.

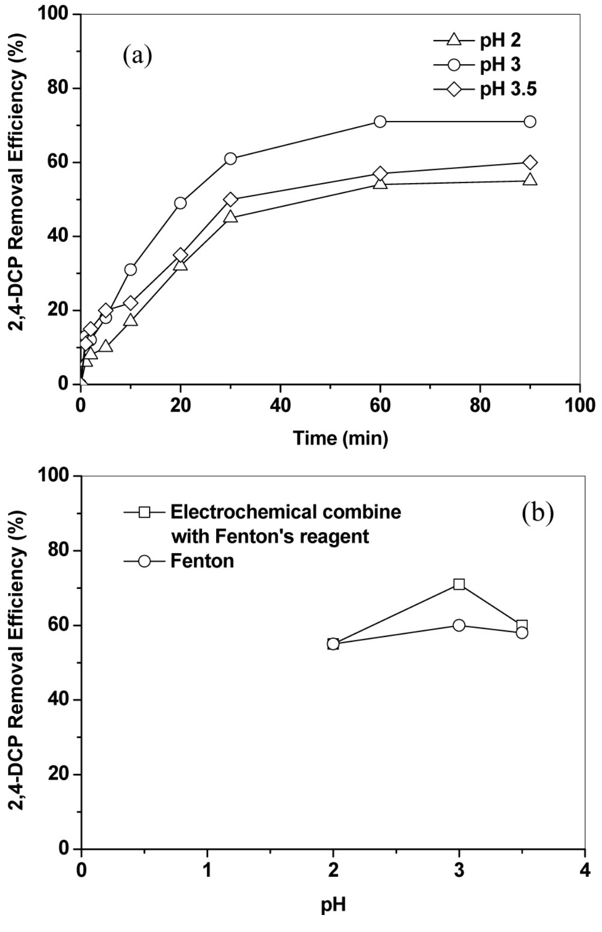

Fig. 2. Effect of operating pH on 2,4-DCP removal by the electrochemical system combined with the Fenton process ([2,4-DCP] = 1 mM, $[Fe^{2+}]$ = 0.1 mM, $[H_2O_2]$ = 1 mM, electrical current 0.05 mA/cm^2).

Table 2
Effect of operating pH on initial degradation rate of 2,4-DCP by the electrochemical system combined with the Fenton process ([2,4-DCP] = 1 mM, [Fe^{2+}] = 0.1 mM, [H_2O_2] = 1 mM, electrical current 0.05 mA/cm^2)

Operating pH	Removal efficiency (%)	Initial degradation rate (10^{-3} M/min)*
2	55	0.020
3	71	0.083
3.5	60	0.057

* In 20 min of reaction time.

because a smaller steady-state concentration of hydroxyl radicals was attained.

3.3. *Effect of current density*

Effect of current density on the performance of the electrochemical system combined with the Fenton process was investigated in this study as shown in Fig. 3. The result demonstrates that 2,4-DCP removal efficiency depends on the optimum current density. The best value for this experiment was 0.05 mA/cm^2 in terms of the highest 2,4-DCP removal efficiency and energy saving. The optimum current density could help increase the process efficiency with a high initial degradation rate as shown in Table 3. The lower and higher current densities could cause lowering in the initial degradation rate and removal efficiency. The decrease in the removal efficiency was probably due to less amount of electrons for Fe^{2+} regeneration at low current conditions and also scavenging effect from much more Fe^{2+} regeneration at a higher current condition which promoted the regeneration of [Fe^{3+}] to [Fe^{2+}] in the process continuously. It follows from the results that when increasing the current density up to 0.12 mA/cm^2 or more, the removal efficiency had almost the same response. Therefore, the current density of 0.05 mA/cm^2 is suggested to be sufficient in this application.

Table 3
Effect of current density on initial degradation rate of 2,4-DCP by electrochemical system combined with Fenton process ([2,4-DCP] = 1 mM, [Fe^{2+}] = 0.1 mM, [H_2O_2] = 1 mM, pH = 3, electrical current 0.01–0.50 mA/cm^2)

Current density (mA/cm^2)	Initial degradation rate (10^{-3} M/min)*
0.01	0.034
0.05	0.083
0.12	0.065
0.25	0.068
0.50	0.061

*In 20 min of reaction time.

3.4. *Effect of H_2O_2 to Fe^{2+} ratio (H/F ratio)*

H_2O_2 to Fe^{2+} ratio (H/F ratio) (mM/mM) is considered to be a major parameter for 2,4-DCP degradation efficiency. The experimental result indicates that increasing the H/F ratio could accelerate the removal efficiency until reaching the maximum level as reported in Fig. 4. Also, the H/F ratio value at 30 was found to be the best effective H/F ratio as 100% of 2,4-DCP removal efficiency could be achieved by the electrochemical system combined with the Fenton process. The H/F ratios over 30 could not upgrade removal efficiencies. The constant efficiency when using H/F ratios more than 30 indicates that the chemicals might be more excessive than required

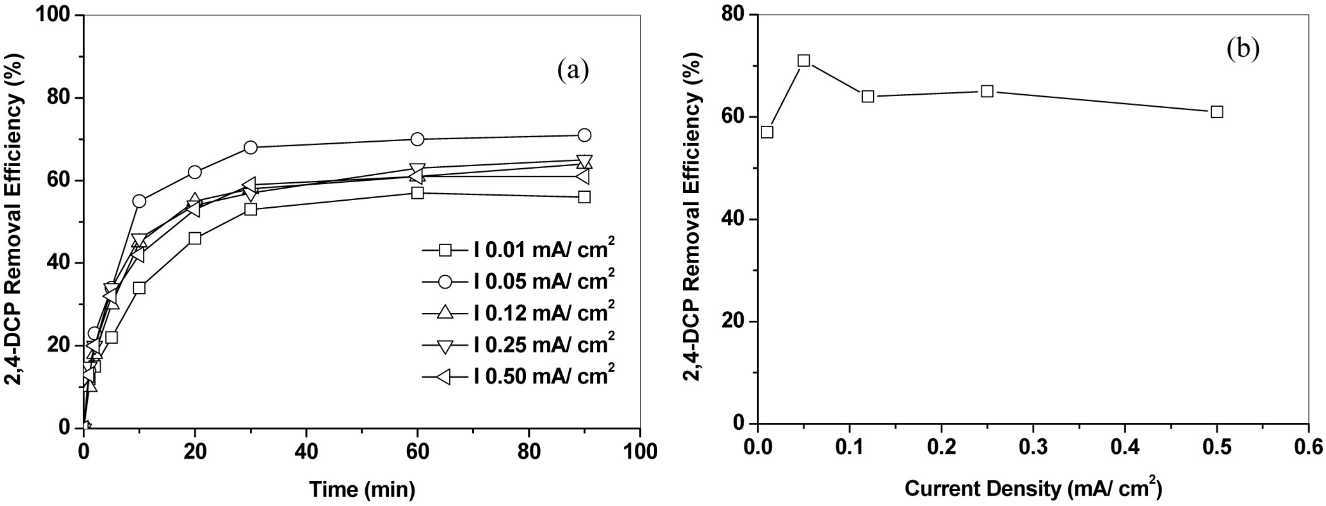

Fig. 3. Effect of current density on 2,4-DCP removal by the electrochemical system combined with the Fenton process ([2,4-DCP] = 1 mM, [Fe^{2+}] = 0.1 mM, [H_2O_2] = 1 mM, pH = 3).

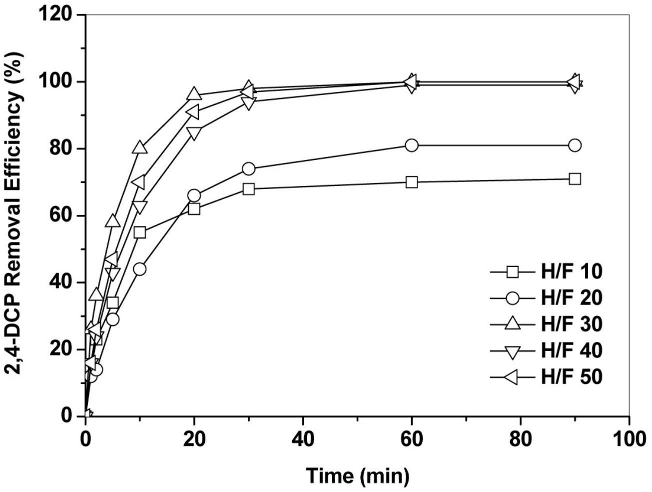

Fig. 4. Effect of H_2O_2 to Fe^{2+} ratios (H/F) on 2,4-DCP removal by the electrochemical system combined with the Fenton process ([2,4-DCP] = 1 mM, [Fe^{2+}] = 0.1 mM, electrical current 0.05 mA/cm², pH = 3).

by this process for 1 mM 2,4-DCP removal. The relative oxidation performance ratio was calculated by using the percentage of 2,4-DCP removal per percentage of H_2O_2 consumed in process. It is used for indicating the oxidation efficiency related to H_2O_2 consuming. From Table 4, the decrease in H_2O_2 effective performance at H/F ratio above 30 might be due to excessive H_2O_2 molecules in the process that make it active in scavenging with other pollutants removal in the process. The relative oxidation performance ratio indicated that the oxidation power of 2,4-DCP removal increased when H/F ratios were less than 30 and decreased after this ratio was more than 30. The data of 2,4-DCP removal per unit consumption of H_2O_2 and relative oxidation performance ratio can confirm that H_2O_2 concentration was the major critical parameter. The efficiencies in COD and TOC removal at various operating conditions are reported in Table 5. The data from the experiment show that under conditions of current density 0.05 mA/cm² with initial Fe^{2+} and H_2O_2 0.1 and 3 mM, respectively at pH 3 could remove 1 mM of 2,4-DCP up to 70%. However, the data from Table 5 also report that 80% of COD and 50% of TOC removal could be obtained when increasing current density to 0.12 mA/cm² and Fe^{2+}, H_2O_2 up to 1 and 20 mM, respectively.

3.5. *Effect of H_2O_2 feeding mode of operation*

Table 4
Effect of H_2O_2 to Fe^{2+} ratios (H/F) on removal efficiency and relative oxidation performance ratio ([2,4-DCP] = 1 mM, [Fe^{2+}] = 0.1 mM, pH = 3, electrical current 0.05 mA/cm²)

H_2O_2 to Fe^{2+} ratios (H/F)	2,4-DCP removal efficiency (%)	2,4-DCP removal per 1 mM H_2O_2 (mM)	Relative oxidation performance ratio
10	71	0.28	1.13
20	81	0.21	1.28
30	100	0.18	1.32
40	99	0.16	1.28
50	100	0.12	1.23

Table 5
Percentages of COD and TOC removal in 2,4-DCP removal by the electrochemical system combined with the Fenton process ([2,4-DCP] = 1 mM, pH = 3)

Current density (mA/cm²)	Fe^{2+} (mM)	H_2O_2 (mM)	COD removal (%)	TOC removal (%)
0.05	0.1	3	40	17
0.05	1	20	60	38
0.12	1	20	80	50

The investigation of 2,4-DCP degradation with two different H_2O_2 feeding modes of operation as one-time initial feeding mode and step feeding mode at a 2-min interval was performed as shown in Fig. 5. The result shows that the feeding mode was dominated at higher current density (at 0.12 mA/cm²). The reason might be that higher current density had more electron supply for Fe^{2+} regeneration. The best degradation efficiency was obtained by using step feeding operation because step feeding operation can generate ·OH continuously and homogeneously. Step feeding operation mode could also help avoid the presence of excessive ·OH concentrations during the earlier oxidation stages and provide a better ability of this species throughout the whole oxidation process. The level of just sufficient amount of H_2O_2 concentration in step feeding operation, as well as the optimum ratio of substrate per H_2O_2 consumption reduce the extension of scavenging reactions involving H_2O_2 and ·OH, thus minimizing H_2O_2 that was inefficient consumption. On the other hand, the Fe^{2+} generation per H_2O_2 ratio was also higher, thus favoring the decomposition of H_2O_2 almost into ·OH instead of O_2. In the lower current density (at 0.12 mA/cm²), the effect of operation feeding modes for both step feeding mode and one-time initial feeding mode did not remark any significant difference in degradation efficiencies. On the other hand, the total organic carbon (TOC) removal also confirmed that the step feeding operation mode was better than the initial feeding mode in mineralization as shown in Fig. 6.

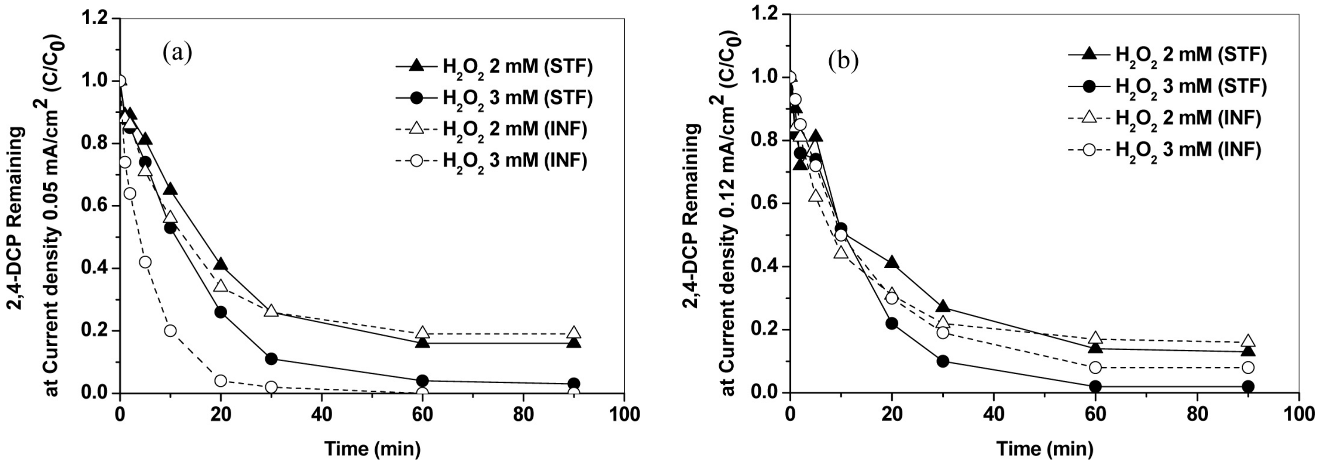

Fig. 5. Effect of H_2O_2 operation feeding mode (step feed; STF, initial feed; INF) on 2,4-DCP removal by the electrochemical system combined with the Fenton process ([2,4-DCP] = 1 mM, [Fe^{2+}] = 0.1 mM, [H_2O_2] = 2 and 3 mM, electrical current 0.05 mA/cm^2 and 0.12 mA/cm^2, pH = 3).

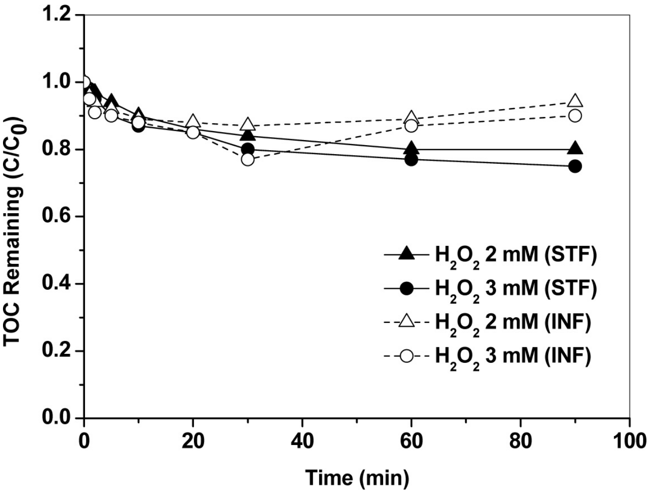

Fig. 6. Effect of H_2O_2 operation feeding mode (step feed; STF, initial feed; INF) on TOC removal by the electrochemical system combined with the Fenton process ([2,4-DCP] = 1 mM, [Fe^{2+}] = 0.1 mM, [H_2O_2] = 2 and 3 mM, electrical current 0.12 mA/cm^2, pH = 3).

3.6. Proposed reaction mechanisms

The reaction pathway of 2,4-DCP oxidation by the electrochemical system combined with the Fenton process for electro-regeneration of ferrous ions is proposed here. High performance liquid chromatography (HPLC) and ion chromatography (IC) were applied to identify and propose the intermediates that might occur among the reactions. The degradation pathway and intermediates occurrence are presented in Fig. 7. The pathway could be proposed as follows: 2,4-DCP was de-chlorinated to 2-chlorophenol, which was further de-chlorinated to phenol. After that phenol was oxidized to hydroquinone by hydroxylation on the C(4)-position of phenol. The formation of hydroquinone might occur by de-chlorinated and hydroxylation from 2-chlorophenol at the same time. Hydroquinone was subsequently dehydrogenated to p-benzoquinone that is known to be a toxic compound at the initial H_2O_2 feeding. In initial feeding conditions, $^{\bullet}OH$ might be empty during the degradation pathway therefore dehydrogenation of hydroquinone to p-benzoquinone dominated. On the other hand, hydroquinone could oxidize to the formation of aliphatic carboxylic acid directly that occurred in H_2O_2 step feed condition. It has been confirmed from this pathway that the step feeding of H_2O_2 might reduce the toxicity possibility rather than initial H_2O_2 feeding. After that the ring cleavage to the formation of maleic acid, the degradation may separate in two-way direction. The first direction is the way of acetic acid formation. The second direction is the way to form oxalic acid and formic acid by hydrogen abstraction. In both degradation pathways, organic acids are directly converted to carbon dioxide and water as final products.

4. Conclusions

The electrochemical system combined with the Fenton process for electro-regeneration of ferrous ions could give high performance in 2,4-DCP oxidation and reduce sludge formation effectively. The best operating conditions were found at operating pH of 3, current density 0.05 mA/cm^2 and the H_2O_2 to Fe^{2+} ratio at 30. Higher efficiency in mineralization could be enhanced when changing the operation mode of one-time initial H_2O_2 feeding to step feeding condition. The step feeding operation could reduce the scavenging effect on the reaction process and decrease a possibility of toxic compound

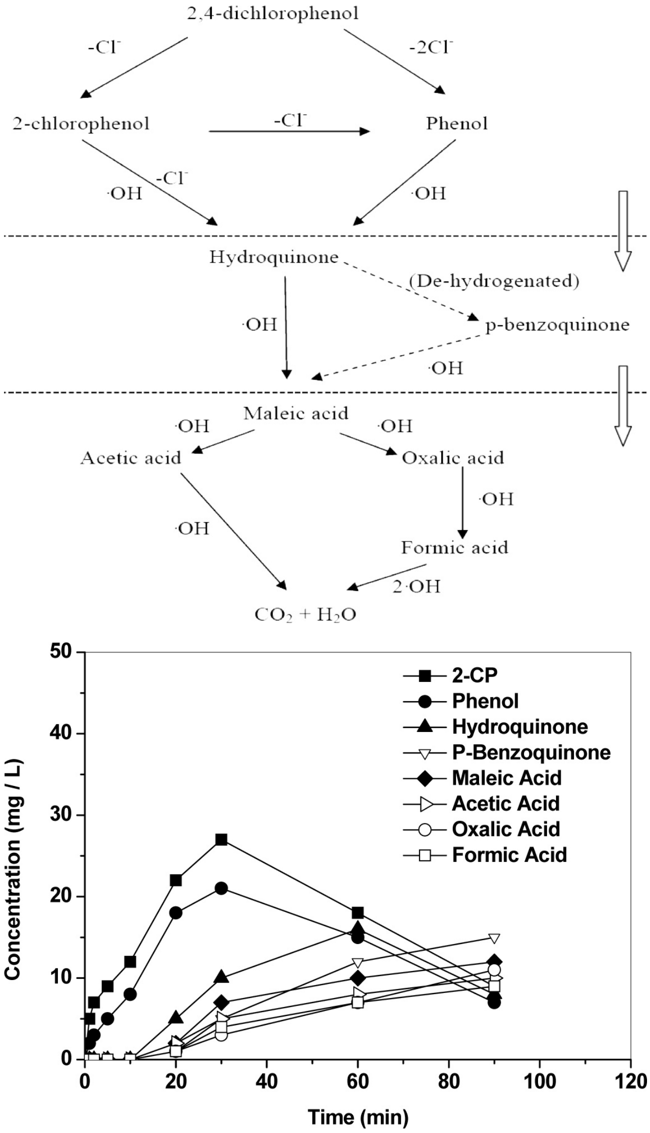

Fig. 7. Proposed reaction pathway and evaluation of intermediate detection on 2,4-DCP degradation by the electrochemical system combined with the Fenton process.

formation from intermediates. A degradation pathway for 2,4-DCP oxidation was proposed on the basis of intermediate compounds that were detected. 2-chlorophenol and phenol were the products of de-chlorination while hydroquinone, p-benzoquinone, maleic, acetic, oxalic, and formic acids were found as the main oxidation intermediates. Moreover, this technology can be challenging and easily scaled up for real world application.

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