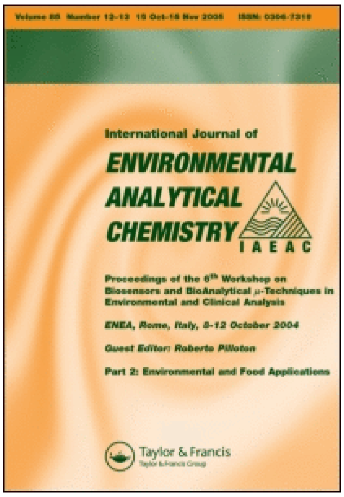

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Electro-Fenton treatment of aqueous Clopyralid solutions

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Electro-Fenton treatment of aqueous Clopyralid solutions

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The removal of Clopyralid (CLPYD) from aqueous solutions was performed by the electro-Fenton process in which hydroxyl radicals are produced electrocatalytically and used to degrade the persistent organic pollutants. The decay kinetics well fitted to pseudo-first order reaction and absolute rate constant of the oxidation reaction of CLPYD was determined as $(4.4 \pm 0.2) \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$. The oxidation intermediates of CLPYD were identified by HPLC and IC analysis. Based on these intermediates, a general oxidation mechanism was proposed in acid medium. Mineralisation ability of the system was followed by the chemical oxygen demand (COD) analysis. The obtained results showed that the CLPYD aqueous solutions were efficiently mineralised during the electro-Fenton treatment.

Keywords: electro-Fenton; AOP; hydroxyl radical; Clopyralid; mineralisation

1. Introduction

Clopyralid (CLPYD, 3,6-dichloro-2-pyridinecarboxylic acid) is a systemic herbicide registered by EPA for control of weeds and woody plants on rangeland and permanent grass pastures, non-cropland areas and rights-of-way. It affects plant cell respiration and growth. This herbicide is generally active in the soil and may be persistent in soils under anaerobic conditions and with low microorganism content. The half-life in soil can range from 15 to more than 280 days. Degradation products have not been identified in the soil up to now [1]. Due to its high solubility in water, this substance is not adsorbed onto soil particles. It may leach into ground-water and constitute a potential threat to the human health and environment. Therefore, the removal of this substance from water resources is very important.

Different treatment techniques such as activated carbon adsorption, chemical oxidation, biological degradation, etc. can be applied to the removal of pesticides from water [2]. But these classical processes are not generally efficient enough in the elimination of such kind of pollutants. For example, activated carbon adsorption involves phase transfer of pollutants without decomposition and thus induces another pollution problem. Classical chemical oxidation using an oxidising agent is unable to mineralise the persistent

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organic pollutants. Concerning the biological treatment, the main drawbacks are: non-efficiency in presence of non-biodegradable and toxic pollutants, slow reaction rates, disposal of sludge and the need for strict control of proper pH and temperature.

Advanced oxidation processes (AOPs) have attracted great attention throughout the last two decades for the treatment of organic pollutants in aqueous solutions due to their ability of total mineralisation [3–8]. These processes involve chemical, photochemical or electrochemical techniques to bring about degradation of organic pollutants. The most widely used AOP is the Fenton's reaction. However, Fenton's reaction has some limitations in application such as the use of large quantities of chemical reagents, large production rates of ferric hydroxide sludge and slow catalysis of the ferrous ions generation [9–10]. Electrochemical AOPs overcome these drawbacks and offer many advantages such as low operational cost and high mineralisation degree of pollutants compared to other known chemical and photochemical ones. In this sense, anodic oxidation and electro-Fenton processes are very commonly used electrochemical AOPs.

Electro-Fenton method is based on the continuous supply of H_2O_2 generated from reaction 1 to a contaminated acid solution containing Fe^{2+} or Fe^{3+} as catalyst [4,11–12]. $^{\bullet}OH$ is then produced in the medium from the Fenton's reaction between ferrous ion and hydrogen peroxide (Equation (2)).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH^{\bullet} \tag{2}$$

$$Fe(OH)^{2+} + e^- \rightarrow Fe^{2+} + OH^- \tag{3}$$

The catalysis of the reaction 2 (which generates hydroxyl radicals) is ensured by Fe^{2+} regeneration, which mainly takes place by the reduction of Fe^{3+} at the cathode (Equation (3)) [13]. Since $OH^{\bullet}$ production does not involve the use of harmful chemicals which can be hazardous for the environment, this process is considered environmentally friendly for wastewater treatment and seems to be promising for the purification of water polluted by persistent and/or toxic organic pollutants [6,7,14].

In this study, we have investigated the removal of CLPYD from water for the first time through its complete conversion to carbon dioxide and water by using electro-Fenton technology. The degradation kinetics was evaluated and degradation by-products were identified.

2. Experimental

2.1 *Materials*

CLPYD was obtained from Riedel-de Haën. Iron(III)sulphate pentahydrate (97%, Across), sodium sulphate (anhydrous, 99%, Across) and potassium sulphate (99%, Fluka) are used as received. Sulphuric acid, (ACS reagent grade, Across), acetic acid (glacial p.a., Across), benzoic acid (99.9%), sodium nitrate (99%) and ammonium nitrate (99%) were purchased from Merck. Oxalic, maleic, fumaric, glyoxylic, acetic, formic and oxamic acids were obtained from Fluka and used without further purification. All solutions were prepared by using pre-distilled 18 $\mu S\,cm^{-1}$ deionised water (Sartorius).

2.2 *Experimental set up*

Experiments were performed at room temperature in a 0.175 L undivided cylindrical glass cell of diameter of 5 cm equipped with two electrodes. The working electrode was a 70 cm^2 piece of carbon-felt (14 × 5 cm). It is placed on the inner wall of the cell covering the totality of the internal perimeter. The counter electrode was a cylindrical Pt net placed on the centre of the cell. Prior to the electrolysis, compressed air was bubbled through the aqueous solutions, which were agitated continuously by a magnetic stirrer (500 rpm). A catalytic quantity (0.1 mM) of ferrous ion was introduced into the solution before the beginning of electrolysis. The applied current was 60 mA for degradation kinetic and by-product determination. 300 mA was used in the mineralisation experiments. The current and the amount of charge passed through the solution were measured and displayed continuously throughout electrolysis by using a DC power supply. Prior to electro-Fenton reaction, the pH of initial solutions was set at 3 by the addition of aqueous H_2SO_4 (1 M). The pH values were measured by a pH glass electrode calibrated with standard buffers at pH values of 4, 7 and 10. The ionic strength was maintained constant (50 mM) by addition of Na_2SO_4.

2.3 *High performance liquid chromatography (HPLC)*

The decay rate of Clopyralid was monitored by high performance liquid chromatography (HPLC) using an Agilent 1100 system equipped with a diode array detector (DAD) and an autosampler. A reversed phase Inertsil ODS-3 (5-µm, 4.6 × 250-mm) column was used in the experiments. The column was thermostated at 40°C. 20 µL of the sample was injected. The column was eluted with a mixture of water (pH: 3) and methanol at 25:75 (v/v) with a flow rate of 0.8 mL min^{-1}. Competitive kinetic experiments were performed at the same mobile phase with a flow rate of 1.0 mL min^{-1}. Detection was performed at 235 nm and 254 nm. Carboxylic acids compounds were identified and quantified by a Supelcogel H column ($\phi = 7.8 \times 300$ mm) with a mobile phase of 4 mM H_2SO_4 at 210 nm. The identification of the intermediates was conducted by the retention time comparison and internal standard addition methods using standard solutions.

2.4 *Ion chromatography (IC)*

The concentrations of chloride, ammonium and nitrate ions released during electrolysis were measured by ion chromatography (Dionex-100 equipped with a conductivity detector). A cationic exchanger column (IonPac® CS12A-Dionex) was used for ammonium ion and an anionic exchanger column (IonPac® AS14-Dionex) was used for nitrate and sulphate ions. The volume of injections was 25 µL. The mobile phase and regenerant solution was 20.0 mM methanesulfonic acid with a flow rate of 0.85 ml min^{-1} and 100.0 mM tetrabuthylammonium hydroxide in the cation analysis, respectively. On the other hand, 30.0 mM NaOH with a flow rate of 0.80 ml min^{-1} and 22.0 mM H_2SO_4 was used in the anion analysis as mobile phase and regenerant, respectively.

2.5 *The chemical oxygen demand (COD)*

The COD analyses of the initial and treated solutions were performed using a standard colorimetric method [15]. Samples were withdrawn from electrolysis solution at different electrolysis time and microfiltered on a hydrophilic membrane (Millex-GV Millipore, pore size 0.22 mm). Oxidation of CLPYD was carried out by potassium dichromate in concentrated acidic medium, in the presence of silver sulfate as catalyst and mercury sulfate. The temperature of the solution was raised to 148°C over a 2h period. The absorbance value of the formed Cr^{3+} during the oxidation process was measured at 600 nm by a UV-visible spectrophotometer (Shimadzu 1610).

3. Results and discussion

3.1 *Decay kinetics of CLPYD in the electro-Fenton process*

The removal of 0.5 mM aqueous CLPYD solutions were investigated in acidic media in the presence of 0.1 mM Fe^{3+} at different applied current values (Figure 1a). As can be seen,

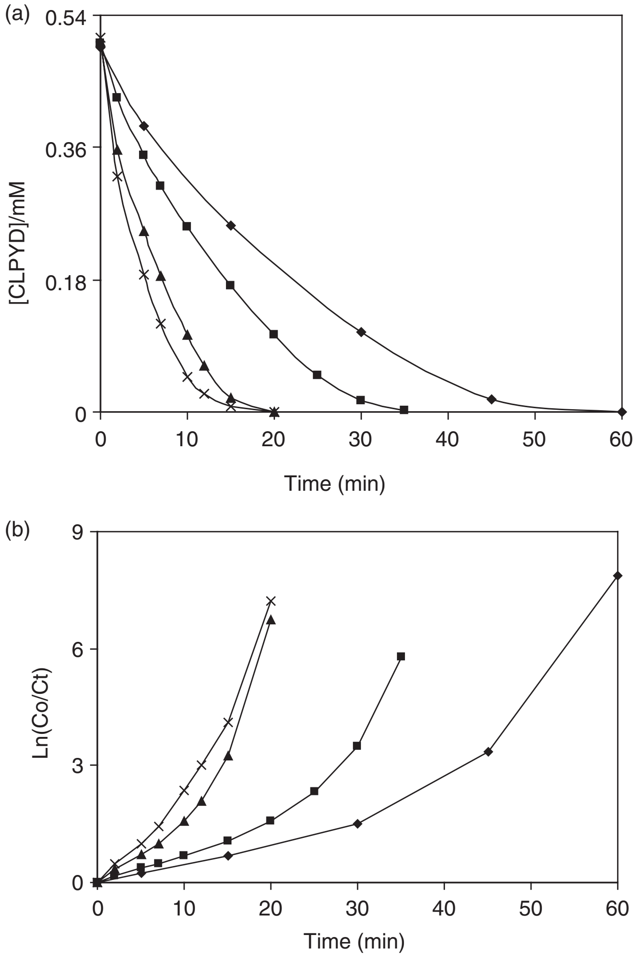

Figure 1. Time-course of 0.5 mM CLPYD at different applied current values (a) and corresponding integrated pseudo-first order lines (b) during the electro-Fenton treatment. I: 60 (◆), 100 (■), 300 (▲) and 500 (×) mA. [Na_2SO_4]: 0.05 M, [Fe^{3+}]: 0.1 mM, pH: 3, T: 35°C, V: 0.15 L.

the concentration of CLPYD was rapidly decreased with electrolysis time in all current values. The obtained results showed that the degradation of CLPYD follows a pseudo-first order reaction kinetic at the initial stage of the electrolysis. After that the degradation rate increased very dramatically at longer electrolysis times (Figure 1b). The reason of this situation may be the formation of active species (chlorine and hypochlorite) by the oxidation of released chloride ions [16,17]. The reaction of these species with CLPYD could increase the degradation rate.

The absolute rate constant value of second order reaction between CLPYD and hydroxyl radicals was determined by the competitive kinetics method [18–19] using benzoic acid (BA, $k_{BA} = 4.3 \times 10^9\,M^{-1}\,s^{-1}$ at 25°C) as standard competition agent. Competitive kinetic experiments were performed in the presence of equal amounts of CLPYD and BA at 60 mA. These experiments permitted to determine the corresponding apparent rate constant values by using integrated first-order kinetics law equation. Finally, the absolute rate constant was calculated as $(4.4 \pm 0.2) \times 10^8\,M^{-1}\,s^{-1}$ by using Equation (4). This value is in agreement with k_{abs} values for hydroxylation reactions of aromatic compounds with hydroxyl radicals [20–21].

$$k_{abs(CLPYD)} = k_{abs(BA)}\,(k_{app(CLPYD)}/k_{app(BA)}) \tag{4}$$

3.2 *Mineralisation of CLPYD by the electro-Fenton process*

Mineralisation of aqueous CLPYD solutions was monitored by the COD analysis during the electro-Fenton treatment. Figure 2 shows the COD values of 1.5 and 3.0 mM CLPYD solutions at 300 mA in the presence of 0.1 mM Fe^{3+}. As can be seen, there is a fast COD removal in both case. The total mineralisation was achieved at almost 120 and 240 min electrolysis for 1.5 and 3.0 mM CLPYD solutions, respectively. The obtained results

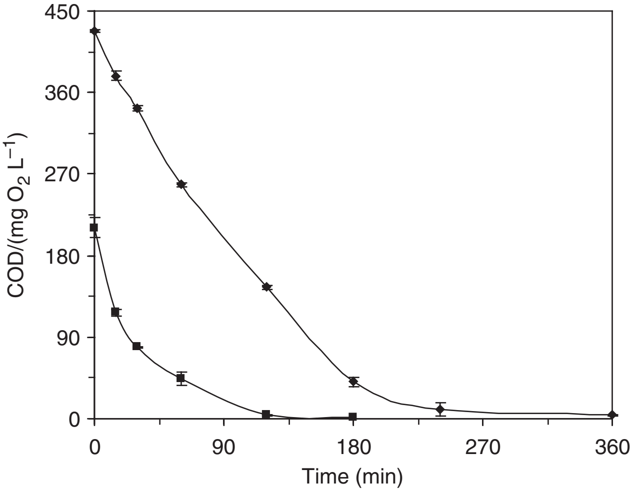

Figure 2. Time-course of COD contents of 1.5 (■) and 3.0 (◆) mM aqueous CLPYD solutions during the electro-Fenton treatment. I: 300 mA, [Na_2SO_4]: 0.05 M, [Fe^{3+}]: 0.1 mM, pH: 3, T: 35°C, V: 0.15 L.

indicate that the electro-Fenton process is very effective way for the removal of this pollutant from water.

3.3 *Determination of oxidation by-products of CLPYD*

HPLC analysis of electro-Fenton treated solutions of CLPYD showed the formation of several by-products but three of them were dominant. The CLPYD peak was rapidly decreased and the peaks corresponding to the by-products were appeared and increased in the first 5 min. After that time, they gradually decreased and completely disappeared in 20 min. This situation indicates that the formed by-products were unstable at the given oxidising conditions. Therefore, they did not accumulate during the electrolysis. Moreover, the gas chromatography-mass spectrometry (GC-MS) analysis of the samples gave no meaningful results.

The formation of short-chain carboxylic acids and inorganic ions is also possible during the electro-Fenton treatment of CLPYD. To determine these intermediates, CLPYD solutions containing 0.1 mM Fe^{3+} were electrolysed at 100 mA. After that, analysis of the samples which were taken from the electrolysis medium at given electrolysis times were performed by HPLC and IC. Formic, oxalic, maleic, fumaric, oxamic and glyoxylic acids were determined as short-chain carboxylic acids (Figure 3). While the formation rates of oxalic, maleic and oxamic acids are very high in the first 90 min, after that time, their accumulation rates gradually decreased.

The ion chromatography analysis indicated the formation of ammonium, nitrate and chloride ions (Figure 4). It can be easily seen that the formation rate of chloride ions is very high in the first 30 min of electrolysis. The released quantity of chloride ions was almost reached to its maximal value at 60 min. After that time, its concentration is nearly

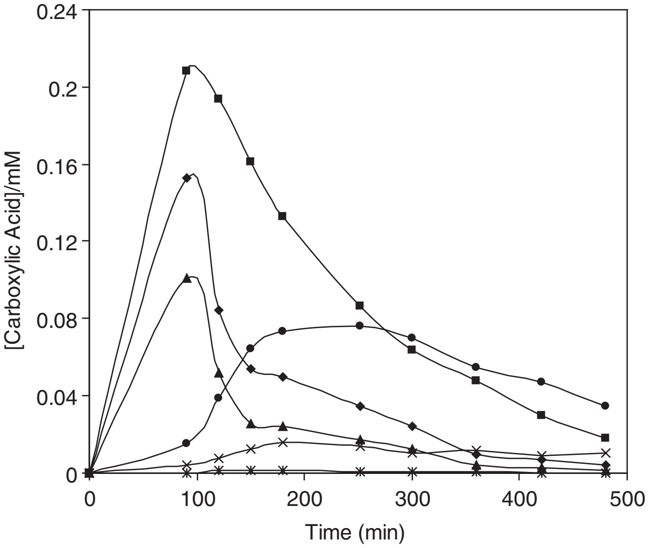

Figure 3. Time-course of short-chain carboxylic acids during the treatment of 0.5 mM CLPYD in the electro-Fenton process. I: 100 mA, [Fe^{3+}]: 0.1 mM, pH: 3, T: 35°C, V: 0.15 L. (●): glyoxylic; (▲): oxamic; (◆): oxalic; (■): maleic; (ж): fumaric; (x): formic acid.

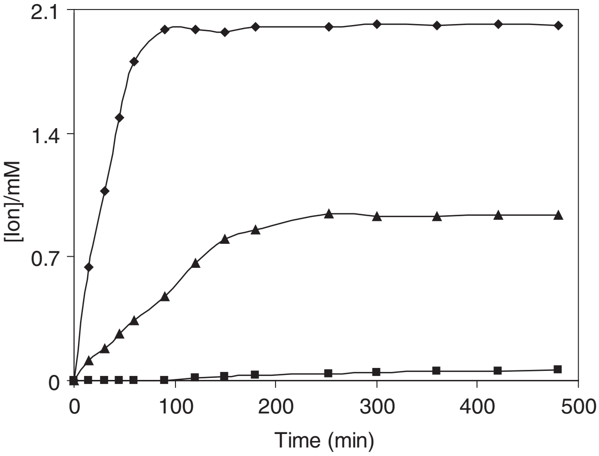

Figure 4. Time-course of inorganic ions formed during the treatment of 1.0 mM CLPYD in the electro-Fenton process. I: 100 mA, [Fe^{3+}]: 0.1 mM, pH: 3, T: 35°C, V: 0.15 L. (▲): ammonium; (◆): chloride; (■): nitrate.

the same. The stoichiometric ratio of initial chlorine was achieved at the end of the electrolysis. Nitrogen atom found in the CLPYD structure was rapidly converted to ammonium ions in the first 30 min of the electrolysis. After that time, ammonium formation rate gradually decreased and reached a steady state value. This behaviour can be explained via the slow degradation rate of oxamic acid (Figure 3) because it forms stable iron complexes and shows resistance to the mineralisation [14]. The formation of nitrate ions can be attributed to the oxidation of ammonium ions on the Pt anode. The obtained concentrations of NO_3^- and NH_4^+ ions showed that 98% of the initial nitrogen was converted to the NH_4^+ ions during the electro-Fenton process. We quantified almost 99% of initial nitrogen as NH_4^+ and NO_3^- ions after 6 h electrolysis.

3.4 *Degradation pathway of CLPYD*

The identified by-products allowed proposing a degradation pathway for the mineralisation of CLPYD by the electro-Fenton treatment in acidic media (Figure 5). The high formation rate of maleic acid and fast accumulation rate of chloride ions during the treatment indicate the electrophilic substitution (ipso attack of OH on C carrying Cl atoms) of the chlorine atoms with hydroxyl radicals. Same behaviour was obtained for picloram before [7]. According to these results, it is supposed that CLPYD is firstly converted to by-products I and II. The oxidation of these by-products with hydroxyl radicals leads to formation of III and IV. The resonance structures V and VI are converted to VII by the substitution reaction with hydroxyl radicals. The formed by-product undergo then the polyhydroxylation reactions followed by the oxidative ring opening reactions to form the short-chain carboxylic acids and inorganic ions. Finally, all organic intermediates are converted into carbon dioxide and water.

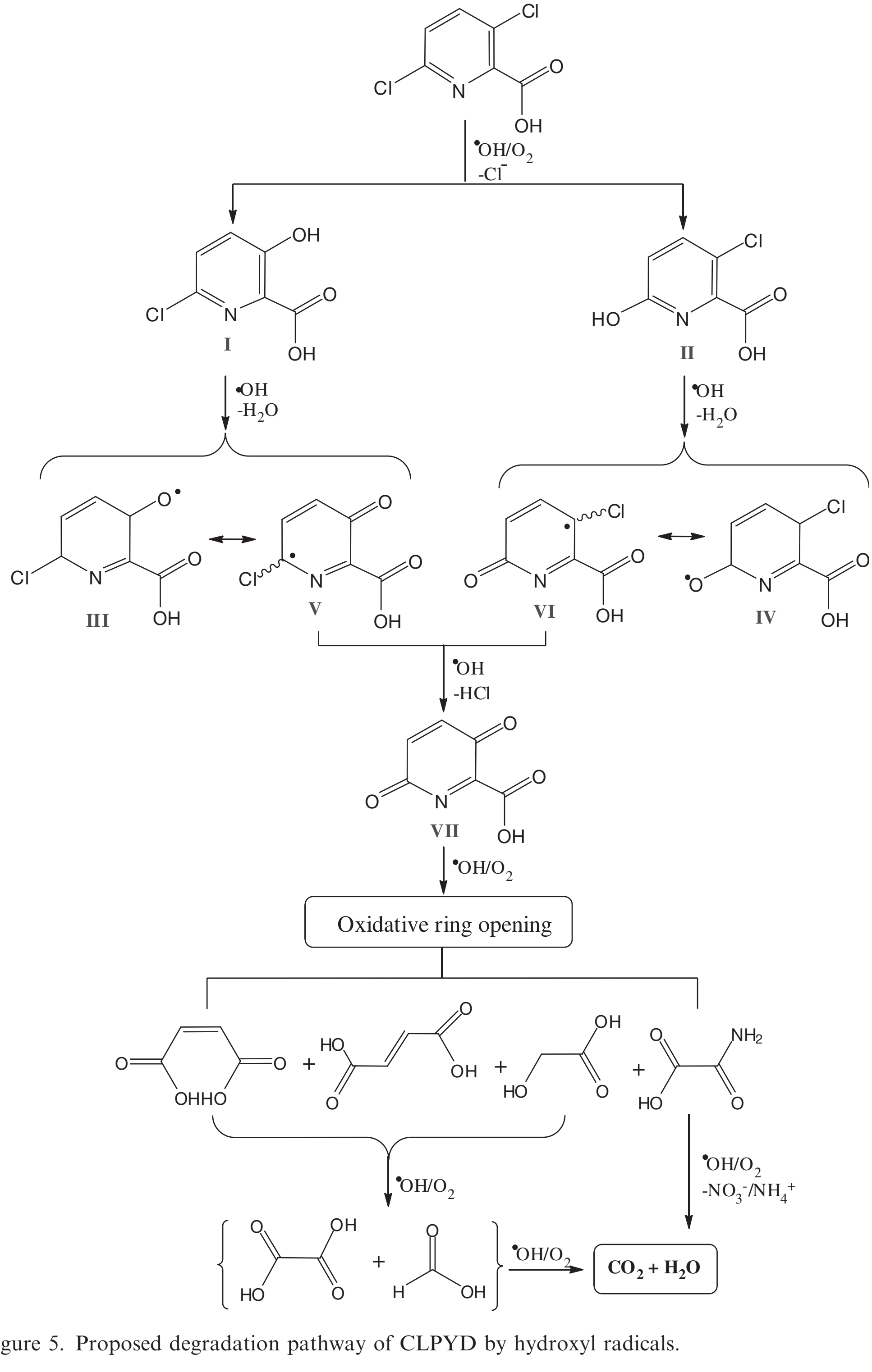

Figure 5. Proposed degradation pathway of CLPYD by hydroxyl radicals.

4. Conclusions

The application of electro-Fenton treatment to the degradation of CLPYD was successfully conducted. Pseudo-first order degradation was observed at the initial stage of the electrolysis. The rate constant of second order reaction between CLPYD and hydroxyl radical was determined as $(4.4 \pm 0.2) \times 10^8\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Some of the degradation intermediates of CLPYD were identified and quantified by HPLC and IC analysis. Mineralisation of solutions was followed by the COD analysis. The obtained results indicated that the overall mineralisation of 3.0 mM CLPYD solution completed within 4 hours.

Acknowledgements

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References

[1] M.C. Corredor, J.M. Rodriguez Mellado, and M.R. Montoya, Electrochim. Acta **51**, 4302 (2006).
[2] World Health Organization Technical Report, *Chemistry and Specifications of Pesticides*, Vol. 899 (WHO, Geneva, 2001).
[3] M.A. Oturan, N. Oturan, C. Lahite, and S. Trévin, J. Electroanal. Chem. **507**, 96 (2001).
[4] B. Boye, M.M. Dieng, and E. Brillas, Environ Sci Technol **36**, 3030 (2002).
[5] E. Brillas, B. Boye, I. Sires, J.A. Garrido, R.M. Rodriguez, C. Arias, P.L. Cabot, and C. Comninellis, Electrochim. Acta **49**, 4487 (2004).
[6] M. Diagne, N. Oturan, and M.A. Oturan, Chemosphere **66**, 841 (2007).
[7] A. Özcan, Y. Şahin, A.S. Koparal, and M.A. Oturan, J. Hazard. Mater. **153**, 718 (2008).
[8] I. Sirés, F. Centellas, J.A. Garrido, R.M. Rodríguez, C. Arias, P.L. Cabot, and E. Brillas, Appl. Catal. B-Environ. **72**, 373 (2007).
[9] C. Walling and A. Goosen, J. Am. Chem. Soc. **95**, 2987 (1973).
[10] J. De-Laat and H. Gallard, Environ. Sci. Technol. **33**, 2726 (1999).
[11] I. Sirés, N. Oturan, M.A. Oturan, R.M. Rodriguez, J.A. Garrido, and E. Brillas, Electrochim. Acta **52**, 5493 (2007).
[12] M.A. Oturan, J. Pinson, J. Bizot, D. Deprez, and B. Terlain, J. Electroanal. Chem. **334**, 103 (1992).
[13] E. Guivarch, S. Trevin, C. Lahitte, and M.A. Oturan, Environ. Chem. Lett. **1**, 38 (2003).
[14] C. Flox, S. Ammar, C. Arias, E. Brillas, A.V. Vargas-Zavala, and R. Abdelhedi, Appl. Catal. B: Environ. **67**, 93 (2006).
[15] American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, 19th ed. (APHA, 1995).
[16] A. Özcan, Y. Şahin, A.S. Koparal, and M.A. Oturan, J. Electroanal. Chem. **616**, 71 (2008).
[17] K. Rajeshwar and J. Ibanez, *Environmental Electrochemistry Fundamentals and Applications in Pollution Abatement* (Academic Press, San Diego, CA, USA, 1997).
[18] K. Hanna, S. Chiron, and M.A. Oturan, Water Res. **39**, 2763 (2005).
[19] S. Ammar, N. Oturan, and M.A. Oturan, J. Environ. Eng. Manage. **17**, 89 (2007).
[20] L.R. Karam, D.S. Bergtold, and M.G. Simic, Free Radic. Res. **13**, 11 (1991).
[21] G.U. Buxton, C.L. Greenstock, W.P. Helman, and A.B. Ross, J. Phys. Chem. **17**, 513 (1988).