

Degradation of picloram by the electro-Fenton process

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Abstract

The degradation of the picloram, a widely used herbicide, has been undertaken by the electrochemical advanced oxidation process, namely electro-Fenton in aqueous solution. This process generates catalytically hydroxyl radicals that are strong oxidizing reagents for the oxidation of organic substances. Degradation kinetics of picloram was investigated. Kinetic results evidence a pseudo first-order degradation, with a rate constant of reaction between picloram and hydroxyl radicals of $(2.73 \pm 0.08) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The effect of applied current and catalyst concentration on the degradation and mineralization of picloram was also investigated. The optimum applied current and catalyst concentration values for the degradation of picloram was determined as 300 mA and 0.2 mM Fe^{3+} , respectively. Mineralization of picloram was followed by the total organic carbon (TOC) analysis. At the end of 8 h of electrolysis, 95% of the initial TOC was removed. Several degradation products were identified by using HPLC, LC–MS, GC–MS, and IC analysis. The identified by-products allowed to propose a mineralization pathway for the picloram degradation. © 2007 Elsevier B.V. All rights reserved.

Keywords: Picloram; AOP; Electro-Fenton; Hydroxyl radical; Degradation

1. Introduction

During the last century, as a result of industrial and agricultural activities, pesticides are the major pollutants of surface water, groundwater and wastewater effluents. This situation is considered as a pervasive problem because these compounds usually have direct adverse effects on the living organisms [1]. Moreover, these compounds are generally toxic and carcinogenic in nature even at low concentrations [2]. For these reasons, intense researches have been paid to remove pesticide loads from wastewater effluents.

Recent progress in the treatment of wastewaters has led to the development of advanced oxidation processes (AOPs). These processes involve chemical, photochemical or electrochemical techniques to bring about chemical degradation of organic pollutants. The most commonly used oxidation processes have H_2O_2 , O_3 or O_2 as the bulk oxidant. The principal active species in such systems is the hydroxyl radical, $\bullet\text{OH}$, a highly oxidizing agent for organic contaminants [3–8]. These radicals react with organic pollutants and thus lead to their degradation by hydrogen abstraction reaction, by redox reaction or by electrophilic addition to π systems [7].

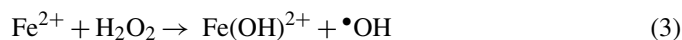
The most commonly used AOPs for the removal of persistent organic pollutants from water is based on the Fenton reaction. Among the different Fenton-like technologies currently available, indirect electrochemical treatment has appeared to be quite efficient in eliminating organic pollutants from aqueous media [9–11]. This technology uses the Fenton reaction as the source of hydroxyl radicals, in which the Fenton reagent, a mixture of H_2O_2 and Fe^{2+} , is produced electrochemically and regenerated throughout the process [12–16] (Eqs. (1)–(3)). Because hydroxyl radical production does not involve the use of harmful chemical reagents which can be hazardous for the environment, this process is environmentally friendly for wastewater treatment and

Abbreviations: AOPs, advanced oxidation processes; HPLC, high performance liquid chromatography; GC–MS, gas chromatography–mass spectrometry; LC–MS, liquid chromatography–mass spectrometry; IC, ion chromatography; UV, ultraviolet; DAD, diode array detector; ESI, electron spray ionization; TOC, total organic carbon; TC, total carbon; BSTFA, *N,O*-bis(trimethylsilyl)trifluoroacetamide; BA, benzoic acid.

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seems to be promising for the purification of water polluted by persistent and/or toxic organic pollutants [7,15].



Picloram (4-amino-3,5,6-trichloro-2-pyridincarboxylic acid) is a herbicide used for broadleaf weed control in pasture and rangeland, wheat, barley, oats, and for woody plant species [17]. Picloram is moderately to highly persistent in the soil environment, with reported field half-lives from 20 to 300 days and an estimated average of 90 days [18]. Photodegradation is significant only on the soil surface and volatilization is practically nil. Degradation by microorganisms is mainly aerobic, and dependent upon application rates. Increasing soil organic matter increases the sorption of picloram and the soil residence time [17]. Picloram is poorly bound to soils, although it is bound better by soils with higher proportions of organic matter [19]. It is soluble in water, and therefore may be mobile [20]. These properties, combined with its persistence, mean it might constitute a risk of groundwater contamination.

The degradation and removal of picloram was investigated by several authors in the literature. Ghauch [21] used zero-valent iron for the degradation of picloram, in this study during 1 h reaction picloram was converted to 4-amino-2-pyridylcarbinol molecule but picloram was not degraded completely to non-hazardous species. Rahman and Muneer [22] used heterogeneous photocatalysis in the presence of different kinds of titanium oxide catalysts. Adsorption process by using the calcinated hydrotalcite [23] and calcinated Mg–Al–CO₃–LDH [24] as sorbents for the removal of picloram from water was also performed.

According to literature there was no study on the degradation and mineralization of picloram by using electro-Fenton process. In this study, we investigated the removal of picloram from its aqueous solution through complete conversion to carbon dioxide and water by the action of hydroxyl radicals which are produced

in the electro-Fenton system. The effect of some operational parameters such as applied current and catalyst concentration on the degradation and mineralization of picloram was also investigated. The rate constant of the hydroxylation of picloram was determined by using competition kinetics. The formed aromatic and inorganic by-products were identified by chromatographic, HPLC, LC–MS, GC–MS, and IC analysis. Finally, a mineralization pathway was proposed for the picloram degradation in aqueous solution.

2. Materials and methods

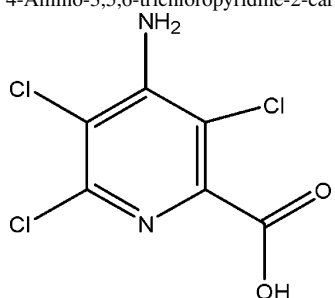
2.1. Materials

Picloram was obtained from Riedel-de Haën. The physicochemical properties of picloram were seen in Table 1. Iron(III)sulphate pentahydrate (97%, Across) and sodium sulphate (anhydrous, 99%, Across) were used as catalyst and supporting electrolyte, respectively. Benzoic acid (99.9%, Merck), sulphuric acid (ACS reagent grade, Across), acetic acid (glacial p.a., Across), and potassium hydrogen phthalate (Nacalai tesque Inc.) were obtained as a reagent grade. Sodium nitrate (99%) and ammonium nitrate (99%) were obtained from Merck and used as standard for the IC analysis. Sodium hydroxide and methanesulfonic acid were used as eluent and tetrabutylammonium hydroxide and sulphuric acid were used as regenerant in the ionic chromatography (IC) analysis. *N,O*-bis-(Trimethylsilyl)trifluoroacetamide (BSTFA, Varian) was used as a derivatization agent for GC–MS analysis. Oxalic, glyoxylic, glycolic, formic, and oxamic acids were obtained from Fluka. All the reagents are commercially available as analytical grade and used without further purification.

2.2. Procedures and equipment

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 50 cm² piece of carbon-felt (10 cm × 5 cm). It is placed on the

Table 1
Physicochemical properties of picloram

Chemical name	4-Amino-3,5,6-trichloropyridine-2-carboxylic acid
Chemical structure	
Molecular weight	241.48 g/mol
Water solubility	430 mg/L at 25 °C
Melting Point	Decomposes at 215 °C
Octanol/water partition coefficient (log <i>P</i> _{ow})	1.9
Adsorption coefficient (<i>K</i> _(oc) = concentration adsorbed/(concentration dissolved % organic carbon in soil))	16

inner wall of the cell covering the totality of the internal perimeter. The counter electrode was cylindrical Pt gauze 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 of ferric ion was introduced into the solution before the beginning of electrolysis. The applied current was 60, 100, and 200 mA for degradation kinetic, by-product determination, and mineralization experiments, respectively. The current and the amount of charge passed through the solution were measured and displayed continuously throughout electrolysis by using a DC power supply (HAMEG Instruments, HM8040-3). Prior to electro-Fenton reaction, the pH of initial solutions was set at 3 by the addition of aqueous H_2SO_4 because this value was reported as the optimal pH value for the electro-Fenton experiments [25,26]. The pH values were measured by a pH glass electrode calibrated with standard buffers at pH values of 4, 7 and 10. IONcheck45 model (Radiometer) pH-Ion meter was employed for pH measurements. The ionic strength was maintained constant (50 mM) by addition of Na_2SO_4 .

2.3. High performance liquid chromatography (HPLC)

The degradation of picloram 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 $5\ \mu\text{m}$, $4.6\ \text{mm} \times 250\ \text{mm}$ column was used in the experiments. The column was placed in an oven which was thermostated at $40\ ^\circ\text{C}$. The injection volume was $20\ \mu\text{L}$. The column was eluted with a mixture of water–acetonitrile–acetic acid at 64:34:2 (v/v/v) with a flow rate of $1.0\ \text{mL}/\text{min}$. Detection was performed at 254 nm. Carboxylic acid compounds were identified and quantified using a Supelcogel H column ($\phi = 7.8\ \text{mm} \times 300\ \text{mm}$) with a mobile phase of $4\ \text{mM}\ \text{H}_2\text{SO}_4$. The detection was performed at 210 nm. The identification of the intermediates was conducted by retention time comparison and standard addition methods using standard substances.

2.4. Liquid chromatography–mass spectrometry (LC–MS)

The transformation of picloram and by-products were monitored by liquid chromatography–mass spectrometry (LC–MS) using an Agilent 1100LC chromatograph coupled to an Agilent 6300 mass spectrometer with an electron spray ionization (ESI) interface and a heated nebulizer, in the positive mode.

2.5. Gas chromatography–mass spectrometry (GC–MS)

In order to identify the aromatic degradation products of picloram, GC–MS analysis were performed. After the electrolysis, the aqueous solutions were filtered and extracted with dichloromethane and ethyl acetate three times. Then, the obtained extracts were evaporated to a final concentration of 2 mL. BSTFA was used to prepare the trimethylsilyl derivatives of the aromatic intermediates. The final solutions were analysed in a GC–MS system (Thermo Finnigan PolarisQ), equipped with

Wiley and NISTMS libraries. A gradient temperature program at $10\ ^\circ\text{C}\ \text{min}^{-1}$ was performed between 40 and $280\ ^\circ\text{C}$ by using a $25\ \text{m}\ \text{SE-54}$ fused silica capillary column.

2.6. The total organic carbon (TOC)

TOC of the initial and electrolyzed samples was determined with a Shimadzu TOC-V analyzer. The platinum catalyst was used to facilitate the combustion reaction. The carrier gas was oxygen with a flow rate of $150\ \text{mL}\ \text{min}^{-1}$. The detector of the TOC system was a non-dispersive infrared detector, NDIR. Calibration of the analyzer was achieved with potassium hydrogen phthalate (99.5%, Merck) and sodium hydrogen carbonate (99.7%, Riedel-de Haën) standards for total carbon (TC) and inorganic carbon (IC), respectively. The difference between TC and IC gives TOC data of the sample.

3. Results and discussion

3.1. Effect of operational system parameters on the degradation of picloram

The effect of some important system parameters such as applied current and Fe^{3+} concentration on the degradation of the picloram in the electro-Fenton process were investigated.

3.1.1. Applied current

The degradation of picloram was followed by reversed-phase chromatography, where it displayed a well-defined peak at a retention time, $t_{\text{R}} = 11.21\ \text{min}$. Several experiments were performed to investigate the effect of applied current on the degradation of picloram by using different current intensities (Fig. 1). It can be seen from Fig. 1 that degradation rate of picloram was increased by increasing applied current value from 30 to 300 mA. This effect could be explained if the amount of $\bullet\text{OH}$ production in the medium is proportional to the increasing H_2O_2 concentration generated when current rises. The complete degradation of aqueous solution of picloram ($0.125\ \text{mM}/150\ \text{mL}$) was

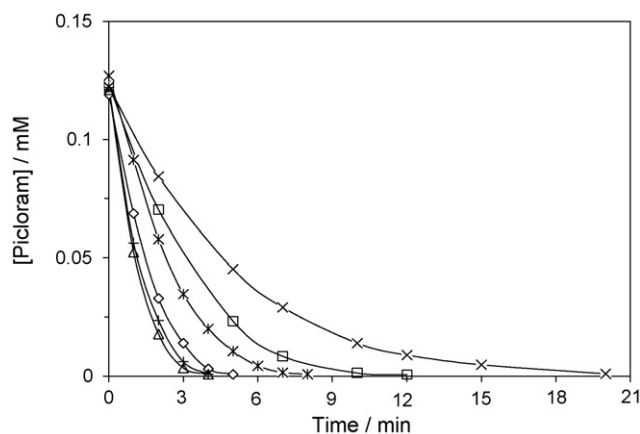


Fig. 1. Degradation kinetics of picloram in acidic media at several current values by electro-Fenton process: (\times) 30 mA; (\square) 60 mA; (\otimes) 100 mA; (\diamond) 200 mA; (\triangle) 300 mA; ($+$) 500 mA. C_0 : $0.125\ \text{mM}$; $[\text{Fe}^{3+}]$: $0.1\ \text{mM}$; $[\text{Na}_2\text{SO}_4]$: $50\ \text{mM}$; V : $0.15\ \text{L}$; pH : 3.

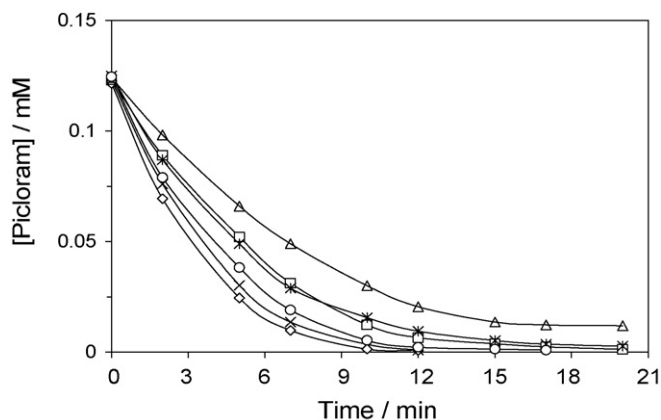


Fig. 2. Effect of catalyst (Fe^{3+}) concentration on the degradation kinetics of picloram in acidic medium at several Fe^{3+} concentration by electro-Fenton process: $[\text{Fe}^{3+}]$: 0.02 mM (\square); 0.05 mM (\circ); 0.1 mM (\times); 0.2 mM (\diamond); 0.5 mM ($*$); 1.0 mM (\triangle). C_0 : 0.125 mM; $[\text{Na}_2\text{SO}_4]$: 50 mM; I : 60 mA; V : 0.15 L; pH: 3.0.

achieved in 4 min at 300 mA constant current. Complete degradation was also obtained in 4, 5, 8, 12, and 20 min in the case of 500, 200, 100, 60, and 30 mA, respectively. These results indicate that the degradation rate of picloram was not changed any more by increasing the applied current value after 300 mA. At higher current values than 300 mA, the $4e^-$ reduction of O_2 leading to the formation of H_2O (Eq. (4)) begin to compete with the formation of H_2O_2 (Eq. (2)). As a result of this situation, the degradation rate remained constant after 300 mA.



3.1.2. The effect of Fe^{3+} concentration

The concentration of catalyst (Fe^{3+}) is another important parameter for the electro-Fenton process. To determine the effect of the catalyst concentration on the degradation of picloram, several electrolysis were carried out in acidic solutions of constant concentration of picloram (0.125 mM) and varying Fe^{3+} concentrations in the range of 0.02–1.0 mM at 60 mA. Fig. 2 shows the results of such a comparison. The degradation rate was found to increase with increasing Fe^{3+} concentration up to 0.1 mM. There was no considerable change in the degradation rate for the concentration values between 0.1 and 0.2 mM. On the other hand, the degradation rate was drastically decreased when the concentration value reached 0.5 mM. In the case of 1.0 mM, the degradation rate was significantly slow. According to the obtained results 0.2 mM was chosen as the optimal concentration value under these conditions and it was used in the rest of the study.

3.2. The rate constant of the reaction between picloram and $\bullet\text{OH}$ radicals

It is now well established that the reaction between organic compounds and hydroxyl radicals follows a pseudo first-order kinetic in the electro-Fenton process at acidic media [7,9,13,15]. The absolute rate constant of picloram degradation by hydroxyl radicals was determined by the method of competitive kinetics

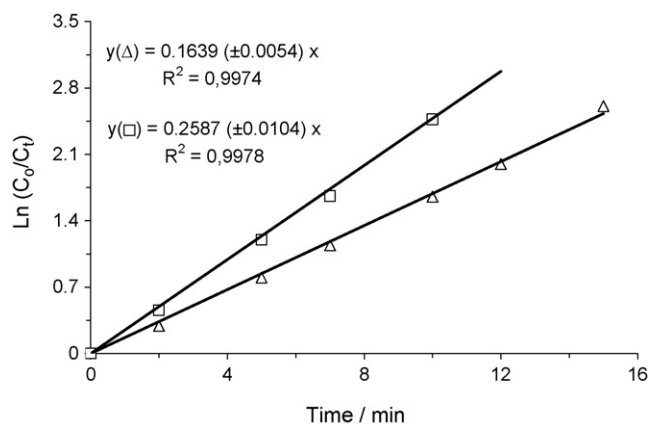


Fig. 3. Concentration–time plot for a competition kinetic between BA (\square) and picloram (\triangle) during an electro-Fenton treatment. $[\text{BA}]_0$: 0.125 mM; $[\text{picloram}]_0$: 0.125 mM; $[\text{Fe}^{3+}]$: 0.2 mM; $[\text{Na}_2\text{SO}_4]$: 50 mM; I : 60 mA; pH: 3.0.

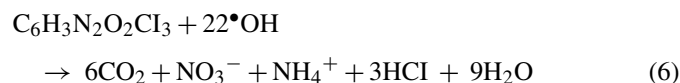
[27] using the competition with benzoic acid (BA) as standard substrate of $k_{\text{BA}} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. For this purpose, competitive kinetic experiments were performed in the presence of equal concentrations of picloram and BA. Assuming a pseudo first-order kinetic for both picloram and BA reactions with hydroxyl radicals (Fig. 3), apparent rate constants are given by the slope of the corresponding straight lines. Apparent rate constant values of picloram and BA were determined as $0.1639 (\pm 0.0054)$ and $0.2587 (\pm 0.0104) \text{ min}^{-1}$, respectively. The absolute rate constant was calculated by using the following equation:

$$k_{\text{abs(picloram)}} = k_{\text{abs(BA)}} \left(\frac{k_{\text{app(picloram)}}}{k_{\text{app(BA)}}} \right) \quad (5)$$

The absolute rate constant of the reaction between picloram and hydroxyl radicals was determined as $(2.73 \pm 0.08) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ according to Eq. (5). This value is in agreement with k_{abs} values for hydroxylation reactions of aromatic compounds with hydroxyl radicals [28,29]. No absolute rate constant for the hydroxylation of picloram was found in literature for comparison.

3.3. The effect of experimental parameters on the mineralization efficiency of picloram

In order to investigate the effects of applied current, Fe^{3+} , and substrate concentration on the mineralization rate of picloram, several experiments were performed at the same conditions. The mineralization reaction of picloram by hydroxyl radicals can be written as follows:



Mineralization of aqueous picloram solution can be monitored by measuring the TOC evolution during electro-Fenton process. The TOC values obtained at different current values during the mineralization of 0.25 mM picloram by the electro-Fenton process is shown in Fig. 4 as a function of electrolysis time. Decrease of TOC can be attributed to the mineralization of

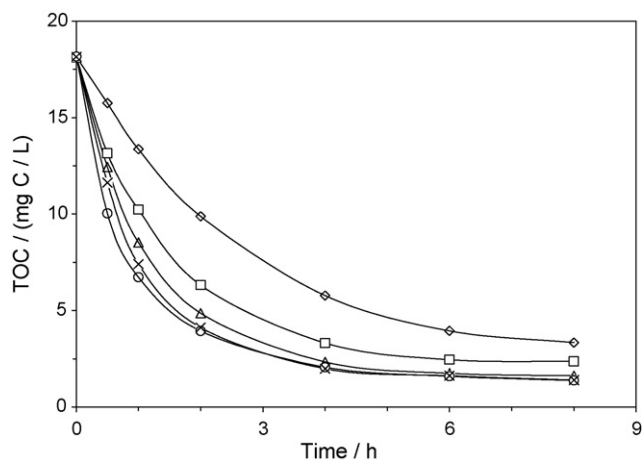


Fig. 4. Mineralization kinetics of picloram in acidic media at several current values by electro-Fenton process: (\diamond) 60 mA; (\square) 100 mA; (Δ) 200 mA; (\times) 300 mA; (\circ) 500 mA. C_0 : 0.25 mM; $[\text{Fe}^{3+}]$: 0.2 mM; $[\text{Na}_2\text{SO}_4]$: 50 mM; V : 0.15 L; pH: 3.0.

picloram by hydroxyl radicals from electrochemically generated Fenton's reagent during the electro-Fenton treatment. It can be seen from Fig. 4 that the mineralization rate of picloram increased by increasing applied current values from 60 to 500 mA. In the first hour of electrolysis, the percentage of the TOC removal were 26.40, 43.64, 53.01, 59.24, and 62.95 for the current values 60, 100, 200, 300, and 500 mA, respectively. After that time, the TOC removal values gradually decreased and reached a steady state. At the end of the 8 h electrolysis, 81.60, 86.99, 90.91, 92.35, and 92.46 of the initial TOC value was removed in the case of current values of 60, 100, 200, 300, and 500 mA, respectively. The mineralization rate was found to increase with increasing applied current value up to 200 mA. There was no considerable change in the mineralization rate below and above this current value. Therefore the optimum current value was found to be 200 mA and used in the following experiments.

The effect of catalyst concentration on the mineralization of picloram was investigated by performing the electrolysis in the presence of different concentration of Fe^{3+} at 200 mA. The evolution of TOC values during the treatment was given in Fig. 5. It can be seen from this figure that the mineralization rate was slow in the presence of 0.02 mM Fe^{3+} . When the concentration of Fe^{3+} was gradually changed from 0.02 to 0.2 mM, a sharp increase was seen in the mineralization rate. Beyond that value, the mineralization rate of picloram was decreased by increasing the Fe^{3+} concentration from 0.2 to 1.0 mM. The inset shows the TOC removal values as a function of catalyst concentration during the electro-Fenton treatment in Fig. 5. TOC removal values were very close to each other in the first 30 min. This means that scavenger effect of the catalyst was not very important in the case of high concentration of organics. On the other hand, after 2 h electrolysis, the obtained TOC removal values showed that the scavenger effect of catalyst reached a significant state. As mentioned above, the TOC removal value reached its maximum in case of 0.20 mM catalyst concentration. These results can be explained by using the side-reactions (Eqs. (7)–(9)) between the

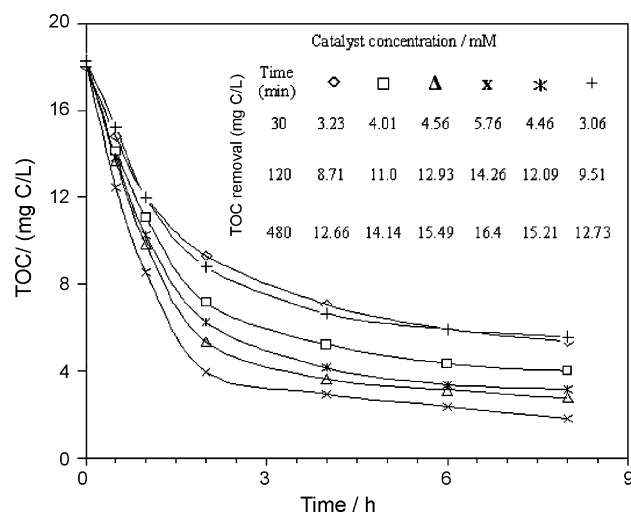


Fig. 5. Mineralization kinetics of picloram ($C_0=0.25$ mM) in acidic media at several Fe^{3+} concentration by electro-Fenton process: $[\text{Fe}^{3+}]$: 0.02 mM (\diamond); 0.05 mM (\square); 0.1 mM (Δ); 0.2 mM (\times); 0.5 mM ($*$); 1.0 mM ($+$). $[\text{Na}_2\text{SO}_4]$: 50 mM; I : 200 mA; V : 0.15 L; pH: 3.0. Inset shows the TOC removal values at given time as a function of catalyst concentration.

hydroxyl radical and the catalyst ($\text{Fe}^{2+}/\text{Fe}^{3+}$) occurred during the electro-Fenton process. When the concentration of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions increased in the medium, the percentage of the scavenged hydroxyl radicals from Fe^{2+} ions increased, so the side-reaction (Eq. (7)) between these species was not ignored [30]. Moreover, Fe^{3+} ion could react with H_2O_2 and hydroperoxy radicals (Eqs. (8) and (9)) which decreases the $\bullet\text{OH}$ production rate [31]. It can be concluded from the results that the concentration of the Fe^{3+} is very important for the degradation and mineralization of picloram in the electro-Fenton process.

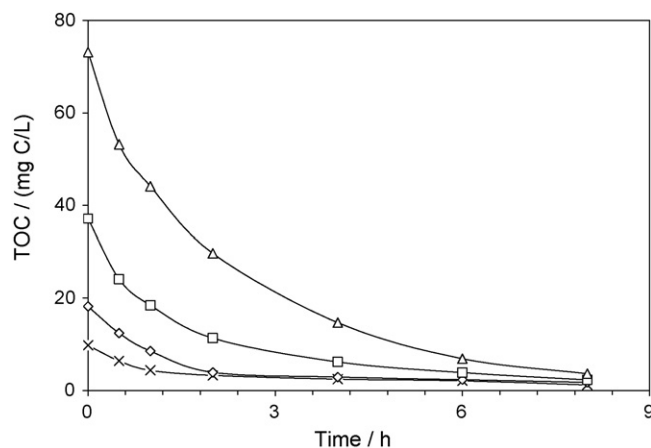
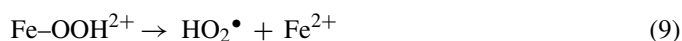
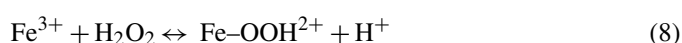


Fig. 6. Mineralization kinetics of 0.125 mM (\times), 0.25 mM (\diamond), 0.5 mM (\square), and 1.0 mM (Δ) picloram at 200 mA in the presence of 0.2 mM Fe^{3+} and 0.05 M Na_2SO_4 by the electro-Fenton process. V : 0.15 L; pH: 3.0.

Table 2
The obtained aromatic by-products during electro-Fenton degradation of picloram at 100 mA constant current electrolysis at pH: 3.0

Compound number	Chemical name	Chemical structure	Retention time, t_R (min)	Molecular ion, M^+	Spectrometric mass fragmentation
I	4-Amino-3,5,6-trichloropyridine-2-carboxylic acid (picloram)		31.70 ^a 19.66 ^{b,c}	241 ^a 384(97), 386(100), 388(36.6)	– 384, 369, 349, 321, 299, 279, 251, 233, 217, 178, 167, 155, 113, 93, 73, 65
II	2,3,5-Trichloropyridine-4-ylamine		13.21 ^b	196(100), 198(96), 200(30.7)	196, 175, 171, 160, 133.1, 107, 98, 73, 63
III	3,5,6-Trichloropyridine-2-carboxylic acid		18.75 ^{b,c}	297(100), 299(99.3), 301(34.4)	297, 277, 255, 217, 197, 168, 125, 114, 93, 73
IV	4-Amino-5,6-dichloro-3-hydroxypyridine-2-carboxylic acid		11.12 ^a 20.72 ^{b,c}	223 ^a 438(100), 440(78.3), 439(33.2), 441(22.9)	– 438, 423, 403, 375, 335, 305, 279, 261, 233, 213, 202, 167, 147, 133, 93, 73
V	5,6-Dichloro-3-hydroxypyridine-2-carboxylic acid		18.92 ^{b,c}	351(100), 352(24.3), 353(67.1),	351, 335, 309, 291, 279, 261, 235, 203, 177, 147, 131, 93, 73

^a Obtained by LC–MS analysis.

^b Obtained by GC–MS analysis.

^c TMS derivatives.

The effect of picloram concentration on the mineralization was studied by electro-Fenton process in the presence of 0.125, 0.25, 0.5, and 1.0 mM picloram in acidic media. TOC evolutions of the above solutions during the electrolysis were given in Fig. 6. As can be seen from the figure, the TOC removal at a given time was dependent on the initial concentration of picloram. For example, after 0.5 h of electrolysis, the initial TOC values of the picloram solutions was reduced from 9.8, 18.2, 37.12, and 73.14 mg L⁻¹ to 6.38, 12.44, 24.13, and 53.21 mg L⁻¹, respectively. As can be seen from the given results, the TOC removal values were increased by increasing the initial TOC of the picloram solution at the same conditions. This situation can be explained by the presence of high amount of organics (picloram and its degradation by-products) in the electrolysis solution at high picloram concentrations. Since the same production of •OH is expected from reactions (1)–(3) in these trials, it seems plausible to consider that its competitive non-oxidizing reactions become slower and more •OH can then react with picloram. On the other hand, TOC removal rate was gradually decreased for all concentration values with electrolysis time. At the end of 8 h electrolysis, TOC of all the systems reached to almost same value. This situation can be explained via the above-mentioned same reason. When the concentration of the organics (picloram and its degradation by-products) was decreased, the side reactions became dominant in the system and consumed the produced hydroxyl radicals so the TOC removal rate was reduced. The residual TOC of the system for all concentration values was arisen from the formed oxalic and oxamic acids during the mineralization of picloram. The oxalic acid is usually the final by-product before complete mineralization during advanced electrochemical oxidation techniques [9,32] because it forms, with the ferric ions, stable ferric-oxalate complexes which are difficult to mineralize by hydroxyl radicals [33]. Consequently, it persists in the medium even after 8 h of treatment.

3.4. Analysis of aromatic degradation products of picloram

The HPLC analysis of electro-Fenton treated aqueous solution of picloram(I) showed the formation of several intermediate

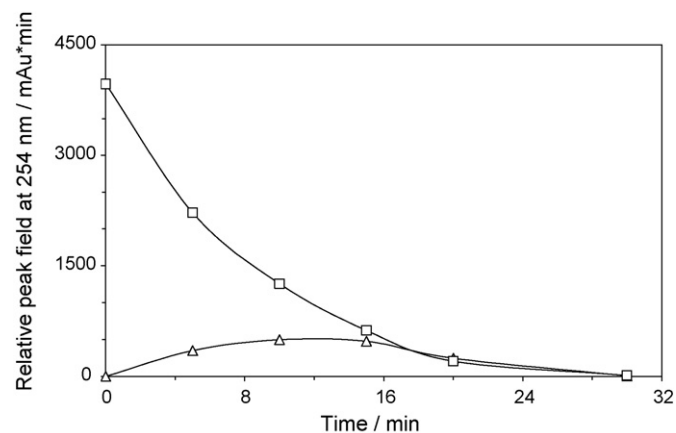


Fig. 7. Time-course of 0.25 mM picloram (□) and its by-product, IV (Δ) during the electrolysis. *V*: 0.15 L; pH: 3; *I*: 100 mA.

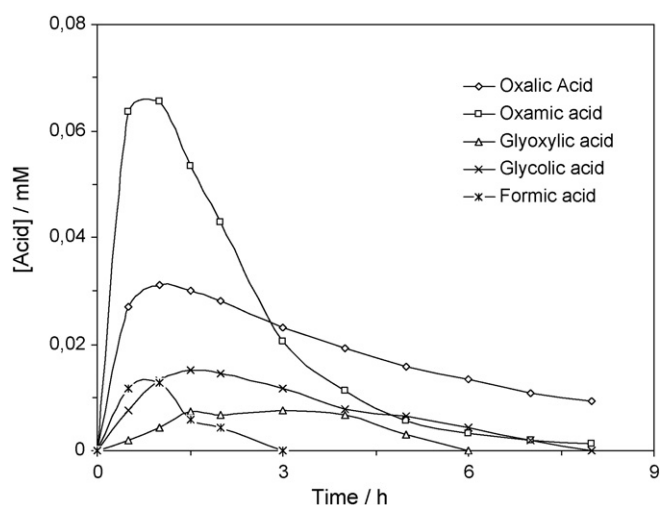


Fig. 8. Time-course of carboxylic acids concentrations during the electro-Fenton treatment of 150 mL of an aqueous solution of picloram in acid medium. [Picloram]₀ = 0.125 mM; [Fe³⁺] = 0.2 mM; *I* = 60 mA.

products. In order to determine these products several analysis were performed by using some chromatographic techniques. The identified products were shown in Table 2. LC–MS analysis showed that the picloram degradation by the action of hydroxyl radicals has led to the formation of several products but a dominant aromatic intermediate with a retention time of 11.12 min. According to its molecular ion, M⁺ (223), this by-product qualified as 4-aminodichlorohydroxypicolinic acid (IV). The transformation of 0.25 mM picloram and evolution of its by-product IV during the electrolysis was given in Fig. 7. One can conclude from this figure that picloram was degraded very rapidly during the electrolysis; on the other hand, the product IV formation starts with the beginning of electrolysis and reached to its maximum concentration in 15 min. After this time its concentration began to decrease and disappeared completely in the first 30 min. Considering the other by-products during the electrolysis, they were produced in small amounts and they degraded very rapidly and they did not accumulate in the system.

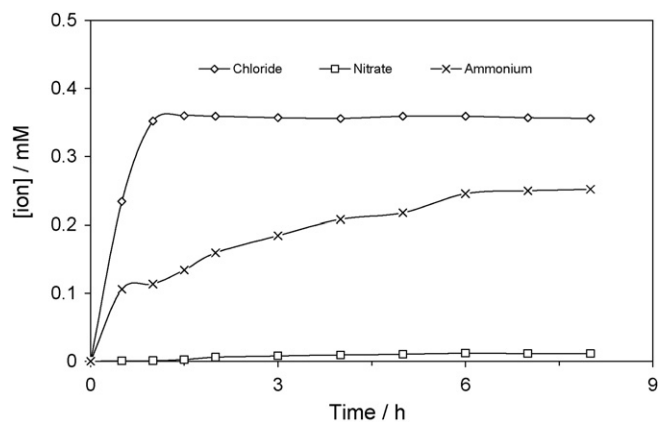


Fig. 9. Time-course of inorganic ions concentrations during the electro-Fenton treatment of 150 mL of an aqueous solution of picloram in acid medium. [Picloram]₀ = 0.125 mM; [Fe³⁺] = 0.2 mM; *I* = 60 mA.

In order to determine the rest of the aromatic by-products formed during the electrolysis, GC–MS analysis were performed. First of all, an aqueous solution of 1.0 mM picloram was electrolyzed at 100 mA for 15 min and the formed aromatic intermediates were extracted by using dichloromethane and ethyl acetate. Finally, the obtained extracts were derivatized by using BSTFA and analyzed in a GC–MS analyzer. The obtained GC–MS results showed that five peaks appearing at retention times (t_R) 13.21, 18.75, 18.92, 19.66, and 20.72 min on the chromatogram. They have been identified based on their molecular ion and mass spectrometric fragmentation peaks (Table 2). Some of the degradation by-products of picloram, II, III, and IV, were reported by Rahman and Muneer [22] in the heterogeneous photocatalysis process by TiO_2 . In that study, the picloram was converted to the intermediates II, III, and IV by the action of the hydroxyl radicals and electron holes found on the TiO_2 particles

during the photocatalytic degradation process. Ghauch [21] also reported the formation of some intermediates and a final product, the 4-amino-2-pyridylcarbinol, by using zero-valent iron reduction process, but the reported intermediates were different from those obtained in our system.

3.5. Identification and evolution of the mineralization end-products: carboxylic acids and inorganic ions

Generation of short chain carboxylic acids is expected from the oxidative breaking of the aryl moiety of aromatic products [10,11,13,26,34]. The evolution of short chain carboxylic acids during the treatment of 0.125 mM picloram solution of pH 3.0 by the electro-Fenton process was followed by ion-exclusion chromatography. The oxalic, oxamic, glyoxylic, glycolic, and formic acids were detected at 7.25, 10.68, 12.22, 15.86, and 17.46 min

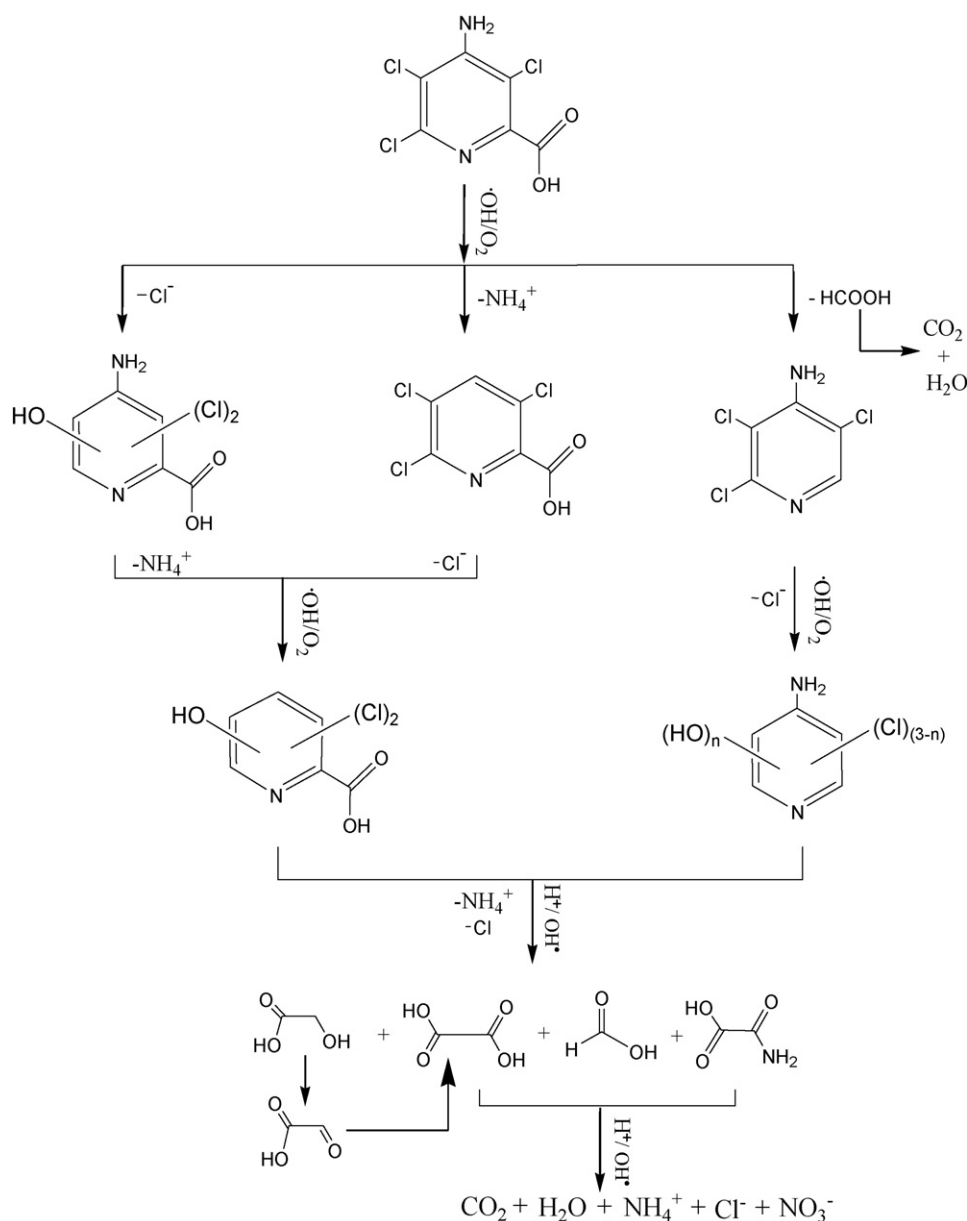


Fig. 10. General reaction sequence proposed for the mineralization of picloram in aqueous acid medium by hydroxyl radicals following electro-Fenton process.

of retention time, respectively, under our analysis conditions. Fig. 8 shows their evolution as function of electrolysis time during electro-Fenton process. As can be seen from Fig. 8, they are generated as soon as the electrolysis is started with a large formation rate for the oxalic, oxamic, glyoxylic, glycolic, and formic acids. The obtained amount of oxamic acid was very high, this situation showed that the most of the initial nitrogen in the picloram structure was converted to the oxamic acid via the oxidative action of hydroxyl radicals. The glyoxylic acid was converted to glycolic and oxalic acids [34]. The decay in the glyoxylic acid concentration was accompanied by an increase in the glycolic and oxalic acid concentrations. Formic acid undergone to the mineralization. Hanna et al. [27] reported that during the mineralization of pentachlorophenol and cyclodextrine they observed some chlorinated carboxylic acids such as dichloromaleic acid. But we did not determine any chlorinated carboxylic acids under our experimental conditions. The reason of this may be the fast releasing rate of the chlorine atoms during the electrolysis (see Fig. 9).

The ion chromatography analysis allowed qualitative and quantitative monitoring of inorganic ions resulting from the mineralization of picloram. The evolution of NO_3^- , Cl^- , and NH_4^+ concentrations during electrolysis is presented in Fig. 9. It was seen from Fig. 9 that the chloride ions were rapidly released from the aromatic moieties. The concentration of released chlorine reached 99% of initial organic chlorine in the first hour of electrolysis. It can be concluded that after 1 h there was no intermediate product which contains chlorine ions. The obtained concentration of NO_3^- and NH_4^+ ions showed that most of the initial nitrogen was converted to the NH_4^+ ions during the electro-Fenton process. In the first 30 min of electrolysis, the formation of ammonium ions were very fast and then its concentration remains constant as 0.106 mM. This value was close to the stoichiometric amount of amino group in the picloram structure. This indicates that the amino group of the picloram was first converted to ammonium ions. After that, the nitrogen of pyridine ring was converted to the oxamic acid which forms stable iron complexes and shows resistance to the mineralization and finally this acid was converted to mainly ammonium and/or nitrate ions [15,35]. The concentration of ammonium ions was found to increase (Fig. 8) with decreasing the concentration of oxamic acid (Fig. 9) during the electrolysis. After 8 h electrolysis, we quantified almost 98% of initial nitrogen of picloram as (4.4% of total) NO_3^- and (95.6% of total) NH_4^+ ions.

3.6. Degradation pathway

A general reaction sequence for the mineralization of picloram in acidic medium by using electro-Fenton process is proposed in Fig. 10. This path involves all intermediates such as aromatic, inorganic, and carboxylic acids. In the case of picloram, all the positions of the aromatic cycle being occupied except the nitrogen of pyridine ring, one can expect an *ipso*-attack on either of chlorine, amino and carboxyl's position. The obtained results indicate that the mineralization of picloram starts mainly with the substitution of the chlorine atoms by the

hydroxyl radicals to form by-product IV. Moreover, amine and carboxyl groups found in the picloram structure were released as ammonium and formic acid to form III and II. The further reaction of III and IV with hydroxyl radicals form the V. On the other hand, the substitution reaction of II with hydroxyl radicals may occur to form more hydroxylated by-products because of the fast releasing rate of chlorine atoms. The degradation of the formed aromatic by-products has led to the formation of aliphatic carboxylic acids such as oxalic, oxamic, glyoxylic, glycolic, and formic acids. The glycolic acid was converted to glyoxylic acid and this product subsequently oxidized to oxalic acid. Moreover, the formic acid was directly converted to carbon dioxide and water. On the other hand, oxalic and oxamic acids form stable complexes with $\text{Fe}^{2+}/\text{Fe}^{3+}$ species and show resistance to mineralization. Finally, all the intermediates were converted to carbon dioxide, water, and inorganic ions, nitrate and ammonium.

4. Conclusions

The Fenton's reagent was electrochemically produced in aqueous solutions, thereby leading to an efficient and continuous $\bullet\text{OH}$ production. This system was successfully applied to the removal of picloram in aqueous medium. Absolute rate constant of hydroxylation reaction of picloram was determined as $k_{\text{abs(picloram)}} = (2.73 \pm 0.08) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The effects of variables on the degradation and mineralization was also investigated. It was found that the degradation and mineralization of picloram largely depend on the Fe^{3+} concentration, applied current, and concentration of picloram.

The degradation of picloram leads to the formation of aromatic reaction intermediates and most of them were identified by GC-MS and LC-MS analysis. Further degradation of the formed intermediates leads to the formation of the short-chain carboxylic acids such as oxalic, oxamic, glyoxylic, glycolic, and formic acids. Ion-exclusion chromatography reveals that oxalic acid is the most persistent final product. Heteroatoms found in the picloram structure were converted to inorganic ions such as Cl^- , NO_3^- and NH_4^+ during the mineralization process. Ion-exchange chromatography indicates that chlorine is most rapidly released to the medium. Complete degradation of picloram and its aromatic by-products were achieved in less than 1 h. The quasi-complete mineralization of 0.25 mM picloram in aqueous solution was achieved in 8 h in this work.

Electro-Fenton process is an economically and environmentally friendly process to remove the toxicity of the recalcitrant compounds in water. The efficiency of this process can be enhanced by coupling with UV irradiation (photoelectro-Fenton) [13,32] and/or biological treatment which is under study in our laboratory.

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References

- [1] D.W. Kolpin, E.M. Thurman, D.A. Goolsby, Occurrence of selected pesticides and their metabolites in near-surface aquifers of the midwestern united states, *Environ. Sci. Technol.* 30 (1) (1996) 335–340.
- [2] International Agency for Research on Cancer (IARC) Monographs, vol. 54, Suppl. 7, IARC, Lyon, France, 1987, pp. 40–51.
- [3] K. Swaminathan, S. Sandhya, A.C. Sophia, K. Pachhade, Y.V. Subrahmanyam, Decolorization and degradation of H-acid and other dyes using ferrous–hydrogen peroxide system, *Chemosphere* 50 (2003) 619–625.
- [4] P.K. Malik, S.K. Saha, Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, *Sep. Purif. Technol.* 31 (3) (2003) 241–250.
- [5] K. Dutta, S. Mukhopadhyay, S. Bhattacharjee, B. Chaudhuri, Chemical oxidation of methylene blue using a Fenton-like reaction, *J. Hazard. Mater.* B84 (2001) 57–71.
- [6] S.H. Lin, C.C. Lo, Fenton process for treatment of desizing wastewater, *Water Res.* 31 (1997) 2050–2056.
- [7] M.A. Oturan, An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants, *J. Appl. Electrochem.* 30 (2000) 475–482.
- [8] P.L. Huston, J.J. Pignatello, Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction, *Water Res.* 33 (1999) 1238–1246.
- [9] M.A. Oturan, N. Oturan, C. Lahite, S. Trévin, Production of hydroxyl radicals by electrochemically assisted Fenton's reagent. Application to the mineralization of an organic micropollutant, pentachlorophenol, *J. Electroanal. Chem.* 507 (2001) 96–102.
- [10] I. Sirés, J.A. Garrido, R.M. Rodríguez, P.L. Cabot, F. Centellas, C. Arias, E. Brillas, Electrochemical degradation of paracetamol from water by catalytic action of Fe^{2+} , Cu^{2+} , and UVA light on electrogenerated hydrogen peroxide, *J. Electrochem. Soc.* 153 (2006) D1–D9.
- [11] I. Sirés, F. Centellas, J.A. Garrido, R.M. Rodríguez, C. Arias, P.L. Cabot, E. Brillas, Mineralization of clofibrac acid by electrochemical advanced oxidation processes using a boron-doped diamond anode and Fe^{2+} and UVA light as catalysts, *Appl. Catal. B: Environ.* 72 (2007) 373–381.
- [12] B. Gözmen, M.A. Oturan, N. Oturan, O. Erbatır, Indirect electrochemical treatment of bisphenol A in water via electrochemically generated Fenton's reagent, *Environ. Sci. Technol.* 37 (2003) 3716–3723.
- [13] E. Brillas, M. Banos, J. Garrido, Mineralization of herbicide 3,6-dichloro-2-methoxybenzoic acid in aqueous media by anodic oxidation, electro-Fenton and photoelectro-Fenton, *J. Electrochim. Acta* 48 (2003) 1697–1705.
- [14] B. Boye, M.M. Dieng, E. Brillas, Degradation of herbicide 4-chlorophenoxyacetic acid by advanced electrochemical oxidation methods, *Environ. Sci. Technol.* 36 (2002) 3030–3035.
- [15] E. Brillas, I. Sirés, C. Arias, P.L. Cabot, F. Centellas, R.M. Rodríguez, J.A. Garrido, Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode, *Chemosphere* 58 (2005) 399–406.
- [16] E. Guivarch, S. Trevin, C. Lahitte, M.A. Oturan, Degradation of azo dyes in water by electron–Fenton process, *Environ. Chem. Lett.* 1 (2003) 38–44.
- [17] W.H. Ahrens (Ed.), WSSA Herbicide Handbook, 7th ed., WSSA, Champaign, IL, 1994, pp. 235–237.
- [18] R.D. Wauchope, T.M. Butler, A.G. Hornsby, P.W.M. Augustijn Beckers, J.P. Burt, The SCS/ARS/CES pesticide properties database for environmental decision-making, *Rev. Environ. Contam. Toxicol.* 123 (1992) 1–157.
- [19] WSSA, Herbicide Handbook, Seventh Edition, WSSA, Champaign, IL, 1994, pp. 10–59.
- [20] H. Kidd, D.R. James (Eds.), The Agrochemicals Handbook, Third ed., Royal Society of Chemistry Information Services, Cambridge, UK, 1991, pp. 10–12 (as updated).
- [21] A. Ghauch, Degradation of benomyl, picloram, and dicamba in a conical apparatus by zero-valent iron powder, *Chemosphere* 43 (2001) 1109–1117.
- [22] M.A. Rahman, M. Muneer, Heterogeneous photocatalytic degradation of picloram, dicamba, and floumeturon in aqueous suspensions of titanium dioxide, *J. Environ. Sci. Health* 40 (2005) 247–267.
- [23] I. Pavlovica, C. Barrigaa, M.C. Hermosinb, J. Cornejob, M.A. Ulibarri, Adsorption of acidic pesticides 2,4-D, clopyralid and picloram on calcined hydrotalcite, *Appl. Clay Sci.* 30 (2005) 125–133.
- [24] L.P. Cardoso, J.B. Valim, Study of acids herbicides removal by calcined Mg–Al–CO₃–LDH, *J. Phys. Chem. Solids* 67 (2006) 987–993.
- [25] J. Pignatello, Dark and photoassisted Fe^{3+} catalysed of chlorophenoxy herbicides by hydrogen peroxide, *Environ. Sci. Technol.* 26 (1992) 944–951.
- [26] M. Diagne, N. Oturan, M.A. Oturan, Removal of methyl parathion from water by electrochemically generated Fenton's reagent, *Chemosphere* 66 (5) (2007) 841–848.
- [27] K. Hanna, S. Chiron, M.A. Oturan, Coupling enhanced water solubilization with cyclodextrin to indirect electrochemical treatment for pentachlorophenol contaminated soil remediation, *Water Res.* 39 (2005) 2763–2773.
- [28] G.U. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\text{O}^\cdot$) in aqueous solutions, *J. Phys. Chem.* 17 (1988) 513–886.
- [29] L.R. Karam, D.S. Bergtold, M.G. Simic, Biomarkers of OH radicals in vivo, *Free Radic. Res.* 13 (1991) 11–16.
- [30] F.J. Benitez, J.L. Acero, F.J. Real, F.J. Rubio, A.I. Leal, The role of hydroxyl radicals for the decomposition of p-hydroxy phenylacetic acid in aqueous solutions, *Water Res.* 35 (2001) 1338–1343.
- [31] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.* 98 (2003) 33–50.
- [32] E. Brillas, E. Mur, R. Sauleda, L. Sanchez, J. Peral, X. Domenech, J. Casado, Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes, *Appl. Catal. B: Environ.* 16 (1998) 31–42.
- [33] B. Boye, M.M. Dieng, E. Brillas, Electrochemical degradation of the herbicide 4-chloro-2-methylphenoxyacetic acid in aqueous medium by peroxi-coagulation and photoperoxi-coagulation, *J. Electroanal. Chem.* 557 (2003) 135–146.
- [34] R. Andreozzi, V. Caprio, R. Marotta, D. Vogna, Paracetamol oxidation from aqueous solution by means of ozonation and $\text{H}_2\text{O}_2/\text{UV}$ system, *Water Res.* 37 (2003) 992–1004.
- [35] C. Flox, S. Ammar, C. Arias, E. Brillas, A.V. Vargas-Zavala, R. Abdelhedi, Electro-Fenton and photoelectro-Fenton degradation of indigo carmine in acidic aqueous medium, *Appl. Catal. B: Environ.* 67 (2006) 93–104.