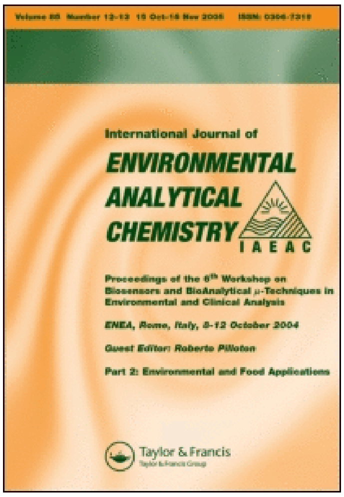

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Treatment of an aqueous pesticides mixture solution by direct and indirect electrochemical advanced oxidation processes

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In the present work, a comparative study on the degradation of a mixture of three pesticides (chlortoluron, carbofuran and bentazon) has been carried out by electrochemical advanced oxidation processes such as anodic oxidation and electro-Fenton using boron-doped diamond (BDD) anode. These processes are based on the in situ production of hydroxyl radical, a highly strong oxidant, which allows the degradation of organic pollutants until their mineralisation into CO_2 and H_2O. Obtained results showed that more than 90% of TOC removal was obtained in 4 h of treatment by both processes. The mineralisation rate was found to be higher for electro-Fenton (BDD) than that of the anodic oxidation. Also, the electro-Fenton (BDD) can mineralise the pesticide solution in 90 min while anodic oxidation requires 150 min. The released inorganic ions, such as chloride, nitrate, sulphate and ammonium, are identified and their kinetic evolution was measured by ion chromatographic analyses.

Keywords: pesticides; anodic oxidation; electro-Fenton; BDD anode; hydroxyl radical, advanced oxidation processes

1. Introduction

Most countries have used pesticides to ensure their food sufficiency and security and maintain agricultural production yields at high levels. However, over time, the intensive use of these chemical products led to their accumulation in waters with consequences on human health. Recently, there is great interest in the remediation of wastewaters containing organic pollutants [1–7] by advanced oxidation processes (AOPs), such as anodic oxidation and electro-Fenton using boron-doped diamond (BDD) electrode [8–14]. These processes are based on the reactivity of hydroxyl radicals ($^{\bullet}OH$) which allow the overall mineralisation of organic pollutants and their breakdown products to CO_2, H_2O and inorganic ions. In anodic oxidation, contaminants are destroyed by reaction with

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hydroxyl radical ($^{\bullet}OH$) generated at the surface of a high O_2 overvoltage anode from oxidation of water in acid and neutral media [15–17]:

$$H_2O \rightarrow {}^{\bullet}OH_{ads} + H^+ + e^- \tag{1}$$

$^{\bullet}OH$ thus produced is a non-selective, very powerful oxidant with ability to react with organics and organometallics until their overall mineralisation (i.e. their conversion into CO_2, water and inorganic ions) is achieved.

In the electro-Fenton process using BDD anode, hydroxyl radicals are formed both heterogeneously at the surface of a high O_2 overvoltage anode such as BDD (reaction 1) and homogeneously from the Fenton's reagent (Fe^{2+} and H_2O_2) according to reaction (2).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad k = 63\,\text{mol}^{-1}\,\text{L}\,\text{s}^{-1} \tag{2}$$

The Fenton's reagent is generated electrocatalytically at the cathode [1,4,18–21] by simultaneous $2e^-$ reduction of dissolved O_2 (reaction 3) and $1e^-$ reduction of iron (III) ions (catalyst) (reaction 4).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E^0 = 0.695\,\text{V/SHE} \tag{3}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^0 = 0.77\,\text{V/SHE} \tag{4}$$

The electrochemically controlled and continuous supply of H_2O_2 and Fe^{2+} from reaction (3) and (4) to the Fenton's reaction (reaction 2) allows to the controlled generation of $^{\bullet}OH$ which react with organic pollutants in order to assume their destruction.

This paper reports a comparative study on the degradation of a pesticides mixture (chlortoluron, carbofuran and bentazone) in synthetic aqueous solutions by two electrochemical advanced oxidation processes, namely anodic oxidation and electro-Fenton, using BDD anode and carbon felt cathode. The decay kinetics of the pesticides and mineralisation kinetics of their aqueous solutions were followed by high performance liquid chromatography (HPLC) analyses and total organic carbon (TOC) measurements during the treatment. Released inorganic ions during treatment were also identified and followed by ion chromatography which constitutes additional data for mineralisation of the pesticides solutions under study.

2. Experimental

2.1 *Chemicals*

Chlortoluron ((3-(3-chloro-4-methylphenyl)-1-1-dimethyl urea)), carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) and bentazone (3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one, 2,2-dioxide) (Figure 1) were reagent grade from Sigma-Aldrich (purity 99.7%). $Fe_2(SO_4)_3 \cdot 5H_2O$ (purity 97%) and Na_2SO_4 (purity 99%) were obtained from Acros. Carboxylic acids were purchased from Acros and Fluka (purity > 98%). Analytical organic solvents were used for HPLC analyses. All solutions were prepared with ultra-pure water obtained from a Millipore Milli–Q system with resistivity $> 18\,\text{M}\Omega\,\text{cm}$ at room temperature.

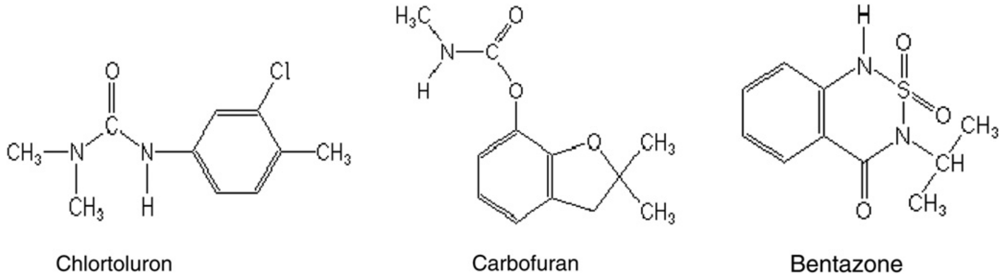
Chlortoluron
Carbofuran
Bentazone

Figure 1. Structure and common name of the pesticides studied.

2.2 *Electrochemical apparatus and procedures*

An EG&G Princeton Applied Research 273A potentiostat/galvanostat was used to perform the electrolyses. Electrolyses were carried out at room temperature in a cylindrical cell of 500 mL equipped with two electrodes. The cathode was a 60 cm^2 carbon felt piece (from Carbone Loraine) and the anode was a BDD thin film (4.5 × 3.1 cm). The pH of solutions was adjusted to 3 by sulphuric acid (H_2SO_4). This value, quite stable along the treatment (H^+ consumed by reaction 2 being compensated by reaction 4), was selected as the optimum one to carry out Fenton's reaction [22,23]. All trials were performed with pesticide solutions containing 50 mM Na_2SO_4 as background electrolyte at room temperature ($23 \pm 2°C$), with stirring by a magnetic bar during the treatment to allow mass transfer. Prior to the electrolysis, compressed air was bubbled for 10 min through the cell to saturate the aqueous solution. Electrolyses were carried out under current controlled conditions. The current remained constant during electrolysis and samples were withdrawn at regular coulometric charges or electrolysis times. The ionic strength was maintained constant by additions of 50 mM Na_2SO_4 to the medium. The fact of adding salts is not a necessary condition for the destruction of organic matter but it improves the conductivity of the medium. For the electro-Fenton (BDD) process, $Fe_2(SO_4)_3 \cdot 5H_2O$ (10^{-4} M) was introduced to the cell as catalyst (Fe^{3+} ions) source just before the beginning of the electrolysis.

2.3 *High performance liquid chromatography (HPLC)*

The evolution of pesticide concentrations was monitored by high performance liquid chromatography (HPLC) using a Merck Lachrom system equipped with L-7455 diode array detector and fitted with a reverse phase Purospher RP-18 5 mm column (4.6 × 250 mm). Detection of chlortoluron, carbofuran and bentazone was carried out at 240, 272 and 225 nm, respectively. The mobile phase was a mixture of water/methanol/acetic acid (48/48/2, v/v/v). It was eluted with a rate of 0.8 mL min^{-1}. Carboxylic acids were identified and quantified by ion-exclusion chromatography using the same HPLC system equipped with a Supelcogel H (7.8 mm × 300 mm) column at 40°C and eluted with a mobile phase of 4×10^{-3} mol L^{-1} H_2SO_4. Detection was carried out at $\lambda = 210$ nm. The flow rate of the mobile phase was set to 0.2 mL min^{-1}.

2.4 *Ion chromatography (IC)*

Inorganic ions (anions and cations) were analysed by DIONEX ICS-1000 ion chromatography equipped with a DS6 conductivity detector (under control through the

Chromeleon SE software), using AS4A-SC, 4 mm × 250 mm anion-exchange column for anion analysis and a CSRS, 4 mm × 250 mm cation-exchange column for cation analysis. The mobile phase was a solution of sodium bicarbonate (1.7 mM) and potassium carbonate (1.8 mM) for anions and sulphuric acid (9 mM) for cations analyses.

2.5 *The total organic carbon (TOC)*

The mineralisation of pesticide aqueous solutions was monitored by the abatement of total organic carbon (TOC) using a Shimadzu VCSH TOC analyser. Samples were acidified with HCl (1% HCl 2 mM) before injection of 50 μL. Calibrations were performed by using the initial chlortoluron solution. TOC measurements were based on the combustion of organics and detection of CO_2 formed by infrared gas analysis method.

3. Results and discussion

3.1 *Effect of pH on the mineralisation efficiency in anodic oxidation*

The electro-Fenton process was generally performed in acidic medium of pH values between 2 and 4, the optimum pH value being 2.8 for hydroxyl radical production from Fenton's reaction [22–24]. Here, we only investigated the optimum pH value for anodic oxidation.

Mineralisation experiments of the pesticides mixture solution by anodic oxidation were conducted at three different pH values: 3, 7 and 12. The pH of treated solutions was adjusted initially to the selected value. The Effect of pH on TOC removal for the mineralisation of the pesticides mixture is shown in Figure 2. Mineralisation efficiency is better at pH = 3 compared to the experiments performed at pH 7 and 12. Mineralisation kinetics are slightly

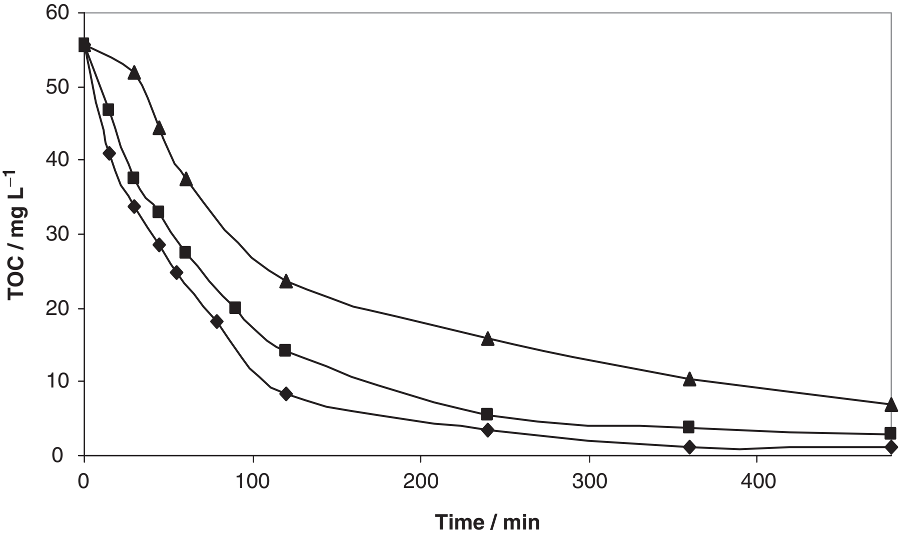

Figure 2. Effect of pH on TOC removal efficiency during mineralisation of the pesticides mixture solution under study by anodic oxidation treatment. pH: 3 (◆), 7 (■) and 12 (▲). $I = 300$ mA, $[Na_2SO_4] = 50$ mM, $V = 250$ mL. $[\text{Chlortoluron}]_0 = [\text{Carbofuran}]_0 = [\text{Bentazon}]_0 = 0.125$ mM.

slower at pH = 7 than pH = 3 and is very poor at pH = 12. Consequently the value of pH 3 was chosen for the experiments.

3.2 *Degradation kinetics*

The anodic oxidation and electro-Fenton (BDD) processes have been used to degrade a mixture of three pesticides: chlortoluron, carbofuran and bentazone. The oxidation power of the two electrochemical processes was highlighted by electrolysing 0.125 mM of each pesticide solution of pH 3 at 300 mA. As shown in Figures 3 and 4, the decay of pesticides concentration with the treatment time is exponential. The disappearance of chlortoluron, carbofuran and bentazone was fast. The chlortoluron, carbofuran and bentazone were completely destroyed after 70, 80 and 90 min of treatment, respectively, by electro-Fenton (BDD) and 90, 120 and 150 min by anodic oxidation processes. For each pesticide under examination the pesticide decay kinetic is faster for electro-Fenton (BDD) than that of the anodic oxidation. The highest decay kinetic of pesticides by electro-Fenton (BDD) can be related to the high production rate of H_2O_2 and consequently a greater amount of $^{\bullet}OH$ produced in the medium from Fenton's reaction (reaction 2) in addition to that generated at the (BDD) anode surface from reaction (1) [11]. The total disappearance of chlortoluron has been achieved in shorter time than carbofuran and bentazone by the two processes. The evolution of the chemical composition and the decay kinetics are similar for the three pesticides. The decay kinetic follows the following order: chlortoluron > carbofuran > bentazone. This order is in agreement with a previous work [6] in which the rate constants of these pesticides with $^{\bullet}OH$ were given as 4.92×10^9, 3.24×10^9, $2.63 \times 10^9\ \mathrm{L\,mol^{-1}\,s^{-1}}$ for chlortoluron, cabofuran and bentazone, respectively.

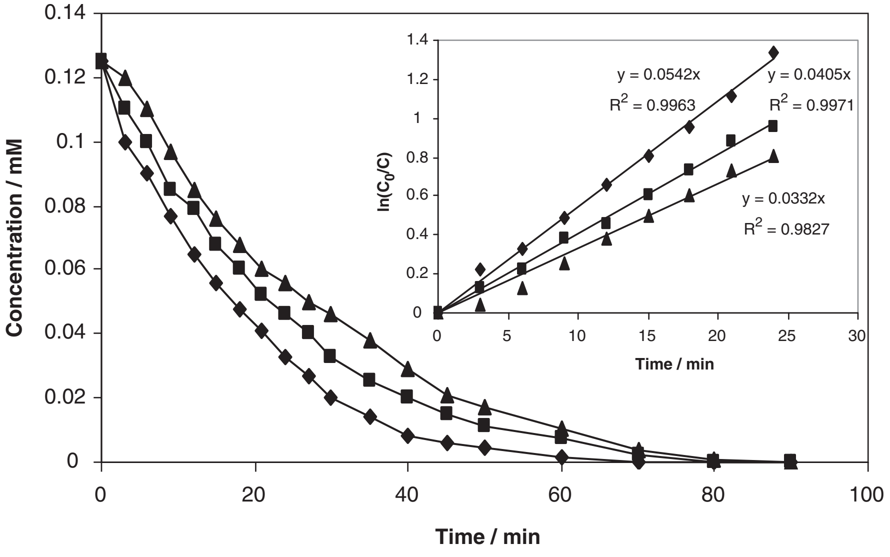

Figure 3. Evolution of the pesticides concentrations during electro-Fenton (BDD) treatment of chlortoluron (◆), carbofuran (■) and bentazone (▲). $[\text{Chlortoluron}]_0 = [\text{Carbofuran}]_0 = [\text{Bentazon}]_0 = 0.125\ \text{mM}$, $I = 300\ \text{mA}$, $[Na_2SO_4] = 50\ \text{mM}$, $V = 250\ \text{mL}$, pH = 3. The insert represents the kinetics analysis $\ln(C_0/C_t) = f(\text{t})$ showing a pseudo first-order reaction kinetics.

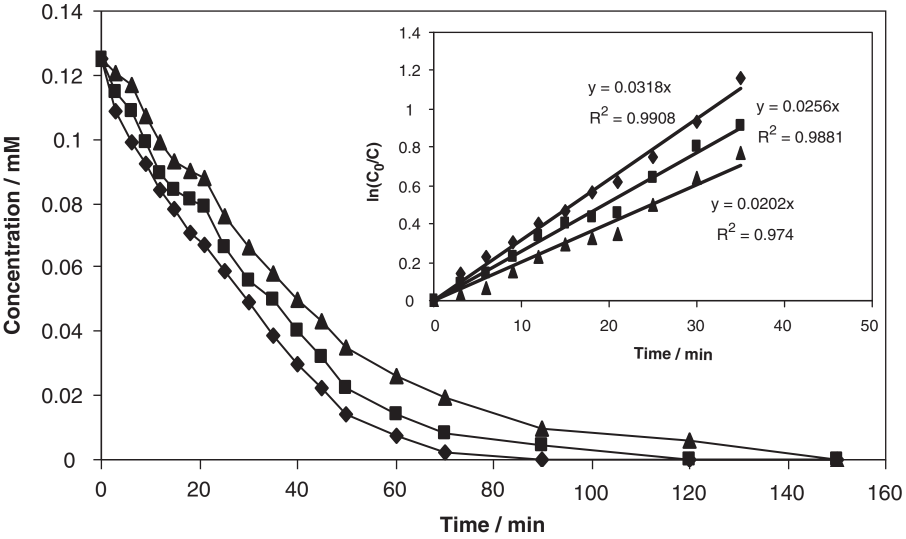

Figure 4. Evolution of the pesticides concentrations during anodic oxidation treatment of chlortoluron (◆), carbofuran (■) and bentazone (▲). $[\text{Chlortoluron}]_0 = [\text{Carbofuran}]_0 = [\text{Bentazon}]_0 = 0.125\,\text{mM}$, $I = 300\,\text{mA}$, $[Na_2SO_4] = 50\,\text{mM}$, $V = 250\,\text{mL}$, pH = 3. The insert represents the kinetics analysis $\ln(C_0/C_t) = f$ (time) showing a pseudo first-order reaction kinetics.

In both processes, the $^{\bullet}$OH formation rate is controlled by the applied current during electrolysis. This rate is limited by the dissolved oxygen concentration in the aqueous solution. These parameters being maintained constant during electrolysis, the $^{\bullet}$OH production rate was also kept constant. As $^{\bullet}$OH is a very reactive species, it does not accumulate in the solution, its concentration takes a steady-state value during treatment. Therefore, the pesticide decay rate can be written as follows:

$$\frac{-d[P]}{dt} = k_{\text{aps}(p)}[P][^{\bullet}\text{OH}] = k_{\text{app}(p)}[P] \qquad (5)$$

where $[P]$ is the pesticide concentration and k_{app} the rate constant of the pseudo-first order reaction. These constants can be calculated from the first-order reaction kinetics law: $\ln([P]_0/[P]_t = k \times t$. The determined apparent rate constant k_{app} for chlortoluron, carbofuran and bentazon oxidation reaction with $^{\bullet}$OH are calculated from insert of Figures 3 and 4 and listed in Table 1 under given experimental conditions of electro-Fenton (BDD) and anodic oxidation processes. The pesticides concentration decays were well fitted to a pseudo-first-order kinetic equation. The excellent linear correlations obtained are depicted in the inset of Figures 3 and 4. This behaviour suggests that the production rate of $^{\bullet}$OH from reaction (1) is constant at the BDD anode during electrolysis, and $^{\bullet}$OH formed are consumed immediately by organics [8].

3.3 *Mineralisation efficiency*

It is well known that reaction intermediates formed during the oxidation of pesticides could be long-lived and even more toxic than their parent compounds. Therefore, it is

Table 1. The apparent rate constant k_{app} for chlortoluron, carbofuran and bentazon determined at the following operating conditions: mixture of three pesticides with [clortoluron] = [bentazon] = [carbofuran] = 0.125 mM, $I = 300$ mA, pH = 3, $V = 0.250$ L.

Process		Chlortoluron	Carbofurane	Bentazone
Anodic oxydation	k_{app} (min^{-1})	0.031	0.025	0.020
	R^2	0.99	0.8	0.97
Electro-Fenton (BDD)	k_{app} (min^{-1})	0.054	0.04	0.033
	R^2	0.99	0.99	0.98

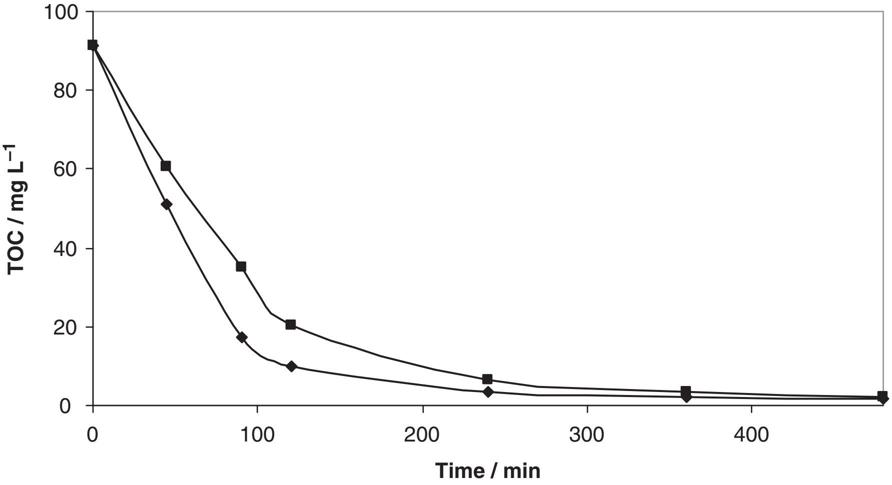

Figure 5. Evolution of TOC removal of pesticides mixture solution during electro-Fenton (BDD) (◆), and anodic oxidation (■). $I = 300$ mA, $[Na_2SO_4] = 50$ mM, $V = 250$ mL. $[\text{Chlortoluron}]_0 = [\text{Carbofuran}]_0 = [\text{Bentazon}]_0 = 0.125$ mM, pH = 3.

necessary to carry out the mineralisation of the pesticides containing solutions in order to eliminate their toxicity at the end of treatment. Mineralisation of the pesticides mixture can be expressed with the total organic carbon (TOC) removal of the solution for electro-Fenton and anodic oxidation processes.

Figure 5 shows that the electro-Fenton (BDD) process presents a TOC removal ratio higher than anodic oxidation. 90% of TOC has totally disappeared in about 120 min for electro-Fenton (BDD) and 240 min for anodic oxidation. The TOC removal values were 98% for electro-Fenton (BDD) and 97% for anodic oxidation at the end of 480 min treatment.

The high mineralisation rate in the early stages of the electro-Fenton (BDD) process can be explained by the quicker reaction of pesticides with the great amount of $^{\bullet}OH$ formed simultaneously from both Fenton's reaction (reaction 2) and water oxidation on BDD anode (reaction 1) [10,11]. A rapid mineralisation kinetic is observed at the first stage of the both treatment due to high reaction rate of $^{\bullet}OH$ with aromatics. TOC removal rate becomes much slower over longer electrolysis times, due to the poor reactivity of $^{\bullet}OH$

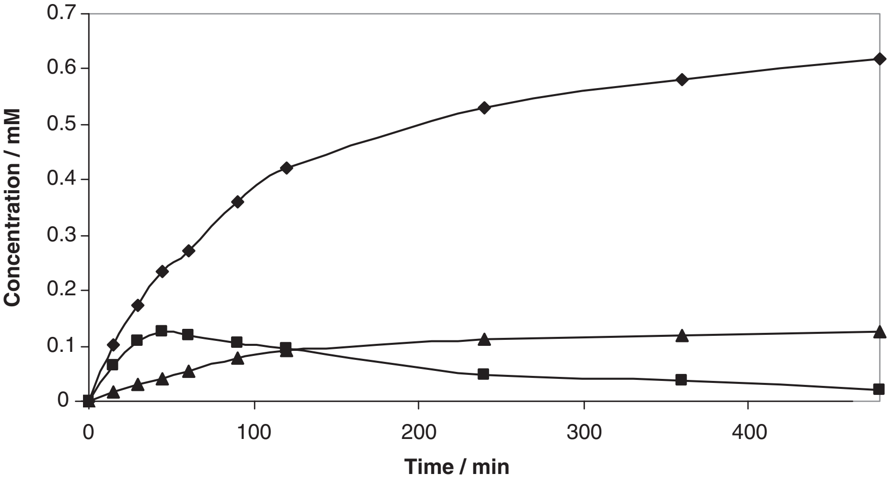

Figure 6. Evolution of inorganic ions concentration formed during the electro-Fenton (BDD) treatment of the pesticides mixture solution. Ammonium (◆), chloride (■) and sulfate (▲). $[\text{Chlortoluron}]_0 = [\text{Carbofuran}]_0 = [\text{Bentazon}]_0 = 0.05\,\text{mM}$, $I = 300\,\text{mA}$, $[NaClO_4] = 0.1\,\text{M}$, $V = 250\,\text{mL}$, $\text{pH} = 3$.

towards short chain aliphatic carboxylic acids formed by ring opening reactions of polyhydroxylated aromatics [6,25,26]. Moreover, the decrease in TOC removal can be influenced by the waste reaction (6) between hydroxyl radicals and Fe^{2+} when the concentration of organic matter becomes weak.

$$^{\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \tag{6}$$

The other weaker oxidants such as ozone and H_2O_2 can be competitively formed with $^{\bullet}OH$ at the BDD anode from the following reactions [8,17]:

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^- \tag{7}$$

$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \tag{8}$$

3.4 *Fate of the hetero-atoms of pesticides*

Figures 6 and 7 show the evolution of chloride, nitrate, sulphate and ammonium ions concentrations that have been released during the treatment of synthetic pesticides aqueous solutions by the electro-Fenton (BDD) and anodic oxidation processes. The ammonium ions were released into the solution faster than the others ions, demonstrating that ammonium ions are the first oxidation by-products for this pesticides. Figures 6 and 7 show that there is no formation of nitrate ions for both the processes. At the beginning of the electrolysis, the production of sulphate ions is rapid and becomes much slower over longer times. The release of ammonium ions (99% for electro-Fenton (BDD) and 97% for anodic oxidation) and sulphate ions (99% for the both processes) were quasi quantitative at the end of the electrolysis. The chloride ions reached their maximum concentration of

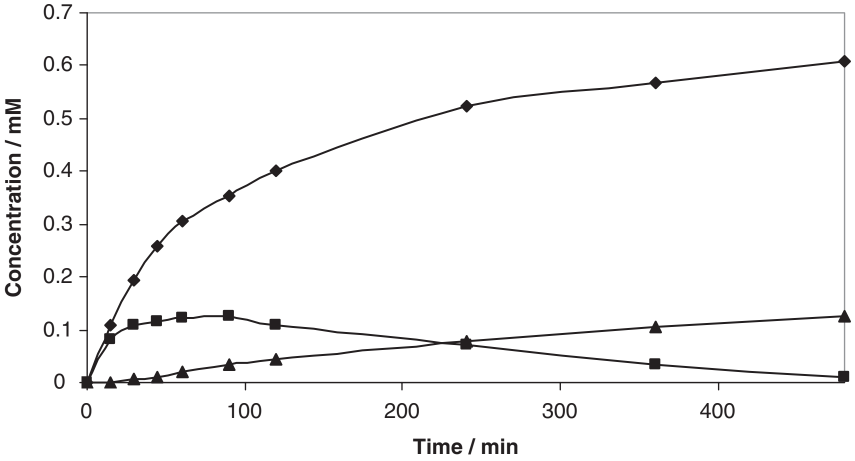

Figure 7. Evolution of inorganic ions concentration formed during the anodic oxidation treatment of the pesticides mixture solution. Ammonium (◆), chloride (■) and sulfate (▲). [Chlortoluron]$_0$ = [Carbofuran]$_0$ = [Bentazon]$_0$ = 0.05 mM, I = 300 mA, [$NaClO_4$] = 0.1 M, V = 250 mL, pH = 3.

0.124 mM (99%) for the both processes after 45 min for electro-Fenton (BDD) and 90 min for anodic oxidation, and further, it is slowly destroyed. The instability of Cl^- under these conditions can be explained by its oxidation to Cl_2 gas on BDD anode according to the reaction (7), as reported for the electrolysis of NaCl aqueous solutions [27]. However, the presence of other chlorine–oxygen ions such as chlorite, chlorate and perchlorate in treated solutions was not detected by ionic chromatography analysis.

$$2Cl^- \rightarrow Cl_2(g) + 2e^- \tag{9}$$

The slower release of chloride, nitrate, sulphate and ammonium ions during longer electrolysis time can be related to their release from slow mineralisation of carboxylic acids or other aliphatic compounds containing these atoms [28].

4. Conclusions

The mineralisation of a mixture of pesticides in aqueous medium by anodic oxidation and electro-Fenton (BDD) processes was studied. The apparent rate constant for the reaction of chlortoluron, carbofuran and bentazone with hydroxyl radicals were found as $k_{app} = 0.031$, 0.025 and 0.020 min^{-1}, respectively, for anodic oxidation and $k_{app} = 0.054$, 0.040 and 0.033 min^{-1}, respectively, for electro-Fenton (BDD) processes. The total organic carbon measurements indicate an efficient mineralisation of the pesticides mixture solutions: 97 and 98% mineralisation for anodic oxidation and electro-Fenton (BDD) process, respectively, after 480 min of treatment. The oxidation rate of initial pesticides and the mineralisation rate of the aqueous solutions were found better for electro-Fenton (BDD) compared anodic oxidation alone. Released inorganic ions concentrations correspond to the theoretical quantities of the heteroatoms present in the initial pesticides mixture solution: 99% for NH_4^+, SO_4^- and Cl^- ions. The chlorine is completely released in the form of Cl^- in a first time and then is slowly oxidised on the anode to Cl_2. These results corroborate with TOC analyses and confirm the overall mineralisation of treated pesticides mixture solutions.

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