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Study of degradation of the fungicide imazalil by electro-Fenton process usingplatinum and boron-doped diamond electrodes

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Abstract

The presence and accumulation of persistent organic pollutants (POPs) in natural waters are emerging pollution issues leading to the disruption of ecosystems and the malfunction of the reproduction of fauna and flora. Among these organic pollutants, imazalil is widely used as a fungicide in agriculture, particularly in Morocco. Its danger lies in its large lifetime in the environment. This work is part of the remediation of persistent organic pollutants (POPs) by alternative techniques such as electro-Fenton process (EF). The results confirmed that this method is effective for the removal of imazalil in water.

*Keywords:*Advanced oxidation, Electro-Fenton, Imazalil, Mineralization, TOC

1. Introduction

Imazalil [1-(2-(2,4-dichlorophenyl)-2-(2-propenyloxy)ethyl)-1*H*-imidazole], an azole fungicide (Figure 1), has been used all over the world for preventing citrus fruits such as lemon, orange, and grapefruit from deteriorating during storage and transportation[1].

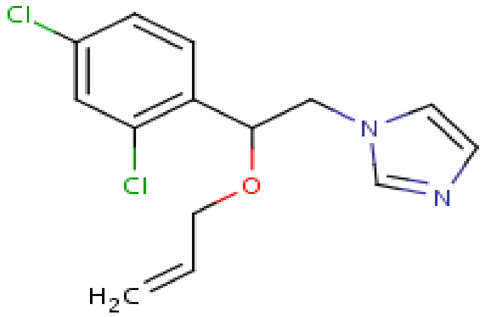


Figure 1: Chemical structure of azole fungicide imazalil.

Imazalil is also widely used in Morocco [2]. To eliminate the potential dangers of this pollutant and its byproducts in aqueous solution, we used the electro-Fenton (EF) process, an electrochemical advanced oxidation process (EAOP) which is a very powerful oxidation method for the degradation of persistent organic pollutants (POPs) in aqueous media [3,4]. It is based on the *in situ* generation of highly oxidizing agent, the hydroxyl radicals,$^{\bullet}OH$ (E° ($^{\bullet}OH/H_2O$) = 2.80V/SHE) in an undivided electrochemical cell under constant current electrolysis. The cell is equippedof a three-dimensional high surface area carbon felt cathode and a platinum (Pt) or boron doped diamond (BDD) anode to generate $^{\bullet}OH$in order to carry out the oxidative mineralization of organic pollutants. $^{\bullet}OH$sare generated homogeneously in the solution through Fenton reaction

(Eq. (1)) for which the Fenton's reagent (H_2O_2 + Fe^{2+}) is electrochemically in situ generated (Eq. (2)) or regenerated from an externally added catalyst (a salt of iron (II) or iron (III)) according to Eq. (3)[5-8].${}^{\bullet}OH$ thus formed isa very strong oxidizing agent and reacts on imazalil leading to its mineralization. The method is optimal at pH 3 for the electrochemical production of hydrogen peroxide [9, 10]. The continuous production of Fenton's reagent (H_2O_2 and Fe^{2+}) in an aqueous medium is provided by the electrochemical reduction of molecular oxygen (Eq. (2)) and of Fe^{3+} formed from Eq. (3)on carbon felt cathode [11-13].

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2O + {}^{\bullet}OH \qquad (1)$$
$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (3)$$

When boron doped diamond (BDD) electrode is used asanode,the efficiency of the process is highly enhanced because of the production of supplementary hydroxyl radicals generated at the surface of BDD anode BDD(${}^{\bullet}OH$) following the Eq. (4) [14-15]:

$$BDD + H_2O \rightarrow BDD({}^{\bullet}OH) + H^+ + e^- \qquad (4)$$

Formed heterogeneous hydroxyl radicals BDD(${}^{\bullet}OH$)are very efficient in mineralization, in particular, in mineralization of short-chain carboxylic acids that are recalcitrant to Pt anode.

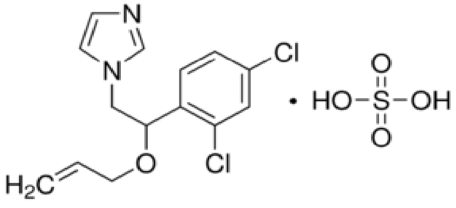
In this work we studied on the oxidative degradation of imazalil and the mineralization of its aqueous solution. Monitoring the oxidative degradation of imazalil and its evolving reaction intermediates during the electro-Fenton treatment and TOC measurements have allowed us to propose a plausible mineralization pathway of this pesticide. The effects of the current intensity and the nature of the anode were also studied. Degradation of imazalil and the evolution of its aromatic intermediates during the oxidation process were monitored by high performance liquid chromatography (HPLC).

2. Materials and Methods

2.1. Chemicals and procedure

Imazalil was obtained from Sigma-Aldrich. Its physicochemical properties have been presented in Table 1. Iron (II) sulfate heptahydrate (Aldrich) was used as a source of ferrous ions as catalyst. Maleic, fumaric and oxalic acids were of analytical grade from Fluka. The anhydrous sodium sulfate and sodium chloride (VWR) were used as supporting electrolytes. Sodium nitrate (VWR), ammonium nitrate and sodium phosphate (Aldrich) were used as standards for analysis by ion chromatography. Organic solvents and other chemicals used for HPLC were reagent grade from l Merck and Fluka.

Table 1: Physical and chemical characteristics of imazalil

Chemical formula:	
Molar mass	395.26 $gmol^{-1}$
Solubility in water at 20 °C	$1.4 g \cdot L^{-1}$
Density	$1.2 g \cdot cm^{-3}$
Saturation vapor pressure at 20 °C	Negligible

Experiments were carried out with a two-electrode system in a 250 mL undivided glass cell. A Pt gauze or BDD (4 cm x 6 cm x 0.2 cm) anode and the carbon felt cathode (14 cm × 5 cm × 0.5 cm) were immersed in 230 mL of 0.1 mM imazalil solution containing 0.1 mM $Fe(SO_4)_3 \bullet 7H_2O$ as source of catalyst and 50 mM Na_2SO_4 as supporting electrolyte. The solution was acidified with H_2SO_4 (1 M) to adjust the pH to 3. Prior to electrolysis, the solution was saturated in $O_2$by bubbling compressed air through the solution. Electrolyseswere conducted under galvanostatic conditions by applying a constant current.

2.2. Analytical techniques

The pH of the solution was measured with a glass electrode calibrated with standard buffers of pH 4, 7 and 10. The decrease of the concentration of imazalil has been monitored by reversed phase HPLC LaChrom (Merck–Hitachi) equipped with a diode array detector (Model L- 7455) equipped with a RP-18 Purosphercolumn, 5 microns, 4.6 mm x 250 mm. This column was eluted isocratically in all experiments with a mobile phase consisting of a mixture of methanol (containing 0.5 % acetic acid) / water (with + 1% acetic acid) 50:50 (v/v) at a flow rate of 0.5 mL min^{-1}. The column temperature was adjusted to 40 °C. The detection was performed at 230 nm.

The short chain carboxylic acids were identified and quantified using an ion exclusion column (H Supelcogel; ϕ = 7.8 mm) of 300 mm lengtheluted with a mobile phase of H_2SO_4(0.1%) at 220 nm. Inorganic ions were analyzed by Dionex ion chromatography (Dionex 1000 equipped with a conductivity detector). An anion exchange column (DionexIonPac - AS14) was used for Cl^- and NO_3^-ions, and a cation exchanger column (DionexIonPac - CS12A) was used for NH_4^+. Mineralization degree of treated solutions was assessed by determining of TOC values with Shimadzu VCSH TOC analyzer following the non-purgeableorganic carbon technique.

3. Resultat and discussion

3.1. Effect of the nature of the anode on the oxidation of imazalil

In order to compare the oxidation power of Pt and BDD anodes, a series of electrolysis of an aqueous solution of 0.1 mM imazalilwas performed using a constant current of 500mA at room temperature (20 ± 2 °C). Figure 1 shows that complete oxidationof imazalil is reachedvery quickly. The complete disappearance of imazalil requires about 12 min with the Pt anode, while the electrolysis time needed for total disappearance of this molecule n is much shorter (8 min) with a BDD anode. This indicates that the EF process is more efficient with the BDD anode. Moreover, in the case of the BDD anode, further hydroxyl radicals are produced on the anodesurface. On the contrary, the Pt anode produces a small amount of radicals that are chemisorbed to the surface. They are less mobile and less available for the oxidation of organic matter.

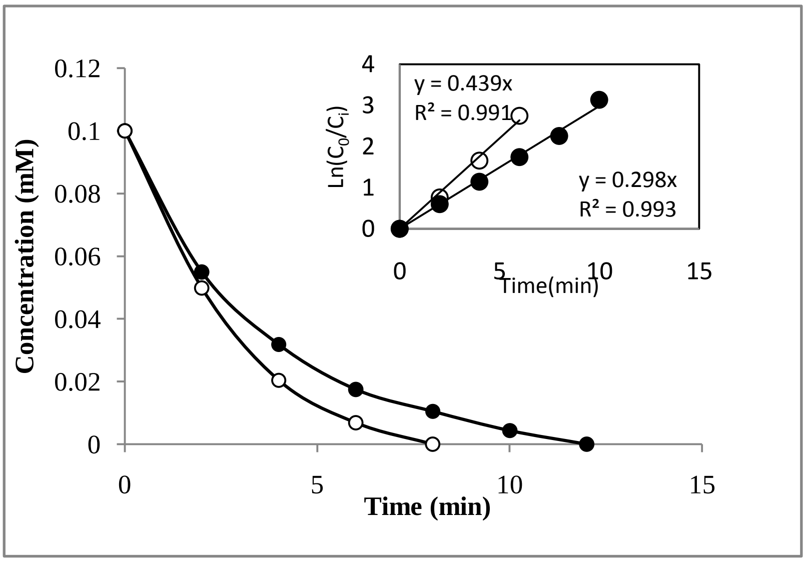


Figure 1: Influence of the nature of the anode on degradation kinetics of imazalil:BDD (○) and Pt (●). [imazalil] = 0.1 mM, [Na_2SO_4] = 50 mM, [Fe^{2+}] = 0.1 mM, pH = 3.The inserted graph presents kinetic analysis following the pseudo-first order reaction kinetics.

3.2. Effect of the current intensity on the degradation of imazalil

Applied current is one of the most important parameters of EF process since the production of Fenton's reagent is monitored by this parameter. The effect of applied current on the concentration decay of imazalil is presented on Figure 2. The electrolysis time required for complete disappearance of imazalilwas shorter when the applied current is high because the enhancement of reactions generating H_2O_2 (Eq. 2)) and Fe^{+2},(Eq. (3)) and consequently a greater amount of produced $^{\bullet}OH$. Current value influence also the generation rate of BDD($^{\bullet}OH$) on the anode surface (Eq. (4)). Figure 2 illustrates degradation of imazalil with time using various applied current values. As seen from this figure, thedecrease in the concentration is exponential indicating that the oxidation reaction of imazalil by hydroxyl radicals take place according to a pseudo-first order kinetics and kinetic analysis of data from this figure allows us to calculate the apparent rate constants (k_{app}) versus applied current values (Table 2). Calculated k_{app} values show that the oxidation of imazalil is optimal for BDD anode at current value of 500 mA.

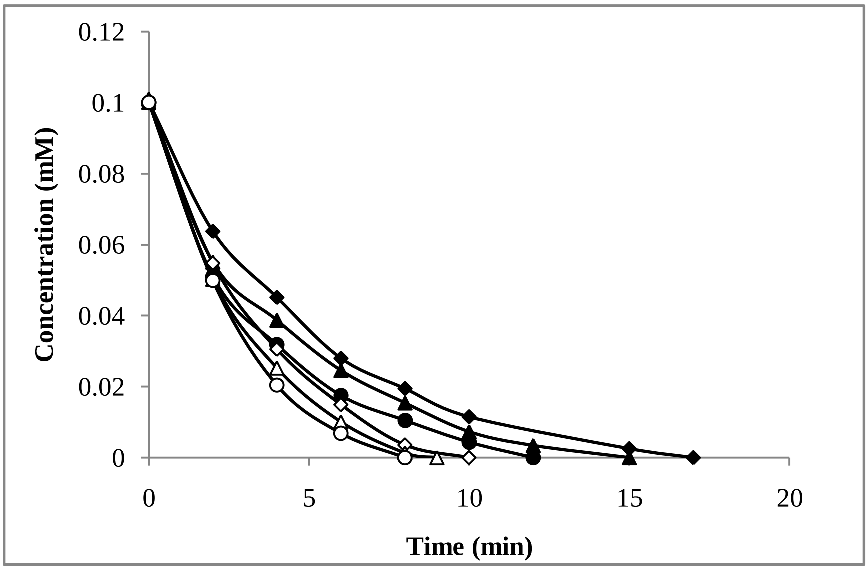


Figure 2: Effect of applied current intensity on the degradation of imazalil during EF process: (♦) Pt-100 mA, (▲) Pt-300 mA, (●) Pt-500mA, (◊) BDD-100 mA, (Δ) BDD-300 mA, (○) BDD-500 mA.[imazalil] = 0.1 mM, [Na_2SO_4] = 50 mM, [Fe^{2+}] =0.1 mM, , pH = 3, volume 230 mL.

Table 2: Evolution of k_{app} values in function of anode material and applied current.

Methods	Anode	I/mA	$k\times10^{-1}$ (s^{-1})	R^2
Electro-Fenton	Pt	100	2.086	0.998
		300	2.472	0.994
		500	2.990	0.990
	BDD	100	3.101	0.997
		300	3,690	0.993
		500	4.399	0.991

3.3. Effect of the nature of the anode and of the current intensity on the mineralization of imazalil

The oxidative degradation of imazalil may lead to formation of toxic reaction intermediate which are present in the solution until complete mineralization. Mineralization of the treated solution provides a safer indication of toxicity, because it means the transformation of the initial pollutant and its intermediates to CO_2 and H_2O. Thus, mineralization of imazalil was followed by measuring the removal of TOC of the treated solution with an initial concentration of 0.1 mM using different current intensities (Figure. 3). This figure shows that the electro-Fenton is able to completely mineralize imazalil with BDD electrode for currents between 300 and 1000 mA. In all cases, after 240 min treatment, more than 97% mineralization is reached. The residual TOC (about 3%) is comprised primarily of short-chain carboxylic acids which have low reactivity with $^{\bullet}OH$.

3.4. Identification and evolution carboxylic acids formed during the mineralization ofimazalil.

Carboxylic acids startto form from the beginning of the electrolysis (Figure. 4a), and reach their maximum concentration between 20-40 min. Beyond this maximum value, the concentration of carboxylic acids decreases rapidly. According to the results given in Figure 4, all the carboxylic acids have been more easily mineralized with the BDD anode compared to Pt anode. As presented in Figure 4bin the case ofPt anode, carboxylic acids are slightly decreasing with the electrolysis time and remain present in the solution after 4 hours of treatment.

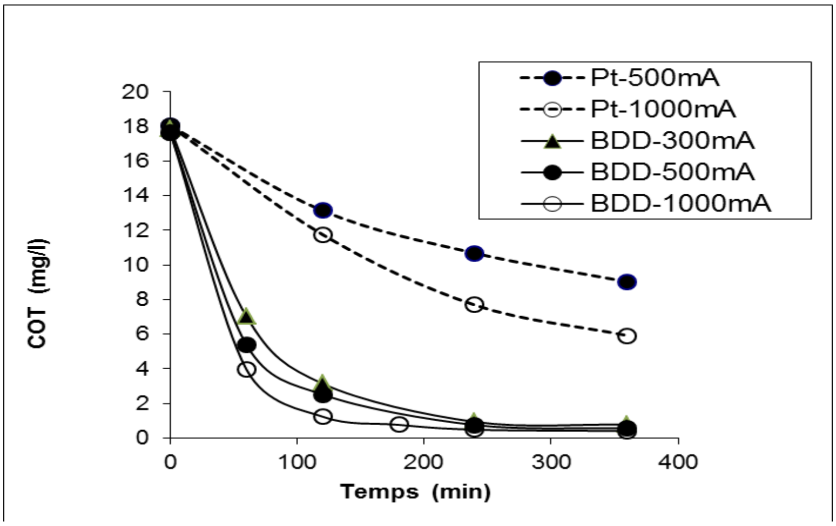


Figure 3: Effect of anode material and current intensity on mineralization of imazalil aqueous solution.[imazalil] = 0.1 mM, [Na_2SO_4] = 50 mM, [Fe^{2+}] = 0.1mM, pH = 3, volume 230 mL.

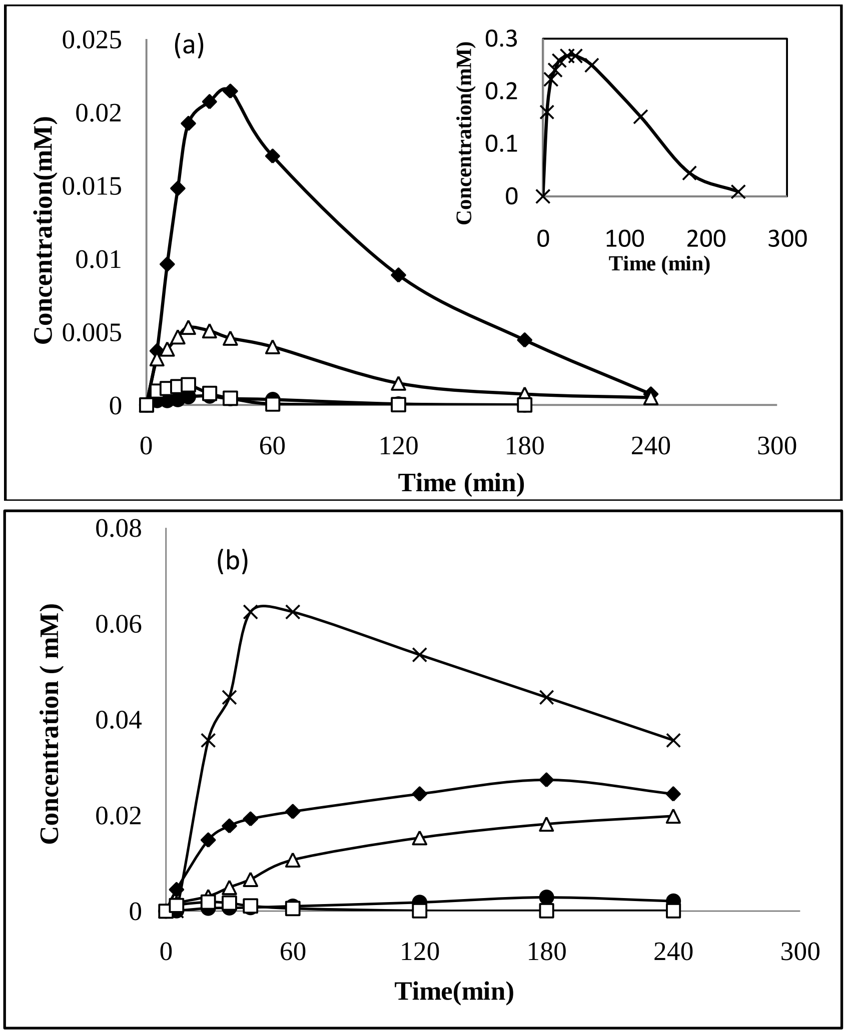


Figure 4: Evolution of carboxylic acids during degradation of imazalil by EF process.(a) BDD anode, (b) Pt anode. (♦) Oxalic acid, (Δ) Oxamic acid, (□) Fumaric acid, (●) Maleic acid, (×) Acetic acid. [Imazalil] = 0.1 mm, [Na_2SO_4] = 50 mM, [Fe^{2+}] = 0.1mM, I= 1000 mA, pH= 3, V = 230 mL.

3.5. Identification and evolution of formed inorganic ions during the oxidation of imazalil

The mineralization process of imazalil involves conversion of the organic matter to carbon dioxide and inorganic ions resulting from the presence of heteroatoms chlorine and nitrogen in the starting molecule [12]. Thus, the release and accumulation of nitrate, ammonium and chloride ions were followed and determinedby ion chromatographyduring the electro-Fenton treatment and results were shown inFigure 5.

The release of Cl^- ions is higher at the beginning of electrolysis (30 to 60 min) with BDD (Figure. 5a), and its concentration reaches its maximum after 60 min electrolysis. Then, its concentration gradually decreases and reaches to a value of 0.03 mM at the end of the electrolysis. This behavior can be explained by oxidation of the Cl^- ion to chlorine (Cl_2) and / or hypochlorite (ClO^-) at the anode according to the following reactions:

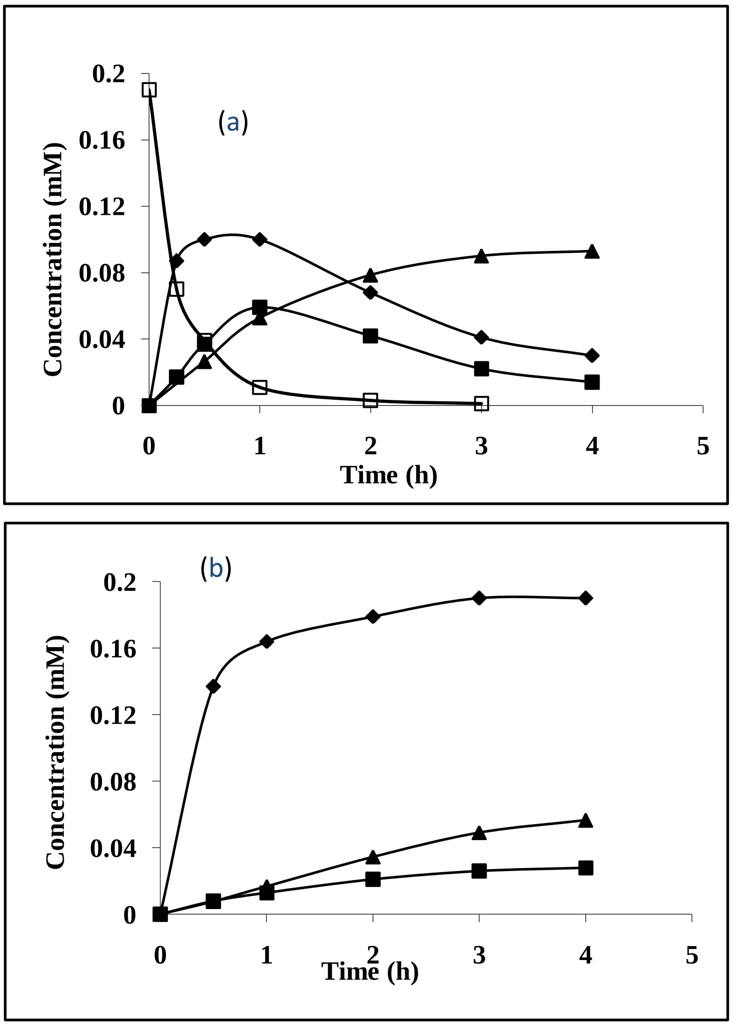


Figure 5: Evolution of inorganic ions during degradation of imazalil by EF process (a): BDDanode, (b) Pt anode.(■): NO_3^-, (□): NO_3^- blank, (▲): NH^{4+}, (♦): Cl^-. [imazalil] = 0.1 mM, [Na_2SO_4] = 50 mM, [Fe^{2+}] = 0.1mM, I = 1000 mA, pH = 3,volume 230 mL.

$2Cl^- \rightarrow Cl_2 + 2e^-$ (5)
$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$ (6)
$HOCl \leftrightarrow H^+ + ClO^-$ (7)

The maximum (theoretical) achievable nitrogen concentration (NO_3^- and NH_4^+) is 0.2 mM (see chemical formula). It is found that the liberation of ammonium and nitrateions is much greater after 1 hour of electrolysis, and the total value reaches to a concentration of 0.152 mM (76% of total nitrogen) (Figure 5a). The total nitrogen balance after 4 h of mineralization is equal to 0.11 mM, representing 55% of the theoretical total nitrogen. The decrease of the concentration of nitrate and ammonium ions can be explained by their oxidation at the BDD anode leading to the formation of gas molecules such as N_2 or NO_x. In order to demonstrate the conversion of nitrate during electrolysis, a 0.2 mM nitrate ion solution was electrolyzed under the same conditions. The results showed that the entire NO_3^- ion was oxidized at 3 hours of electrolysis.

Figure 5b shows the evolution of inorganic ions on Pt anode. In this case, the concentration of Cl^- is 0.19 mM (95% of theoretical chloride), where the concentrations of ammonium and nitrate ions are 0.056 mM and 0.028 mM respectively (45% of theoretical total nitrogen). Two important differences are observed compared with BDD anode. Firstly, there is an accumulation of inorganic ions. It is clear that, the oxidation power of the Pt anode is not sufficient to oxidize these ions. Secondly, the results are far from the theoretical value. This is attributed to the low mineralization rate in the case of the Ptanode (67% after 4 hours of treatment). Thismeans that the solution still containsby-products including the nitrogen atoms.

Conclusion

The results obtained in this study show that the mineralization of aqueous solutions of imazalil with an initial concentration of 0.1 mM (equivalent to 17 mg L^{-1} TOC) is almost complete (more than 97% mineralization) after 4 hours of electro-Fenton treatment using BDD anode. This mineralization rates allows us to highlightthat the EF method is extremely effective for treating waters contaminated with imazalil. Comparison of Pt and BDD anodes for mineralization of imazalil with EF demonstratethe higher efficiency of BDD thanks to formation of highly reactive BDD($^{\bullet}$OH) on its surface that are efficient in oxidation of carboxylic acids. The concentrations of inorganic ions NO_3^- and NH_4^+ are greater with a BDD anode than that with Pt anode, due to the week mineralization rate with the latter .As regards to chloride ions, production kinetics are the same with both electrodes. However, it is observed their accumulation in the solution with Pt anode and its progressive destruction with BDD anode following its oxidation to Cl_2.

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