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Electrochemical Abatement of Analgesic Antipyretic 4-Aminophenazone using Conductive Boron-Doped Diamond and Sub-Stoichiometric Titanium Oxide Anodes: Kinetics, Mineralization and Toxicity Assessment

Soliu O. Ganiyu,^[a] Nihal Oturan,^[a] Clément Trellu,^[a] Stéphane Raffy,^[b] Marc Cretin,^[c] Christel Causserand,^[d] and Mehmet A. Oturan^{*[a]}

The oxidation ability of two prominent eco-friendly electrochemical advanced oxidation processes (EAOPs), namely anodic oxidation with H₂O₂ generation (AO-H₂O₂) and electro-Fenton (EF) for complete abatement of acidic solution of 4-aminophenazone (4-APZ) has been investigated using conductive boron-doped diamond (BDD) and sub-stoichiometric titanium oxide (Ti₄O₇) anodes and carbon-felt cathode. The higher performance of EF compared to AO-H₂O₂ with either anode was demonstrated. In all trials, 4-APZ was completely destroyed, following pseudo first-order kinetics with the rate constant values increasing with applied current and higher values attained with BDD compared to Ti₄O₇ anode at similar conditions. The absolute rate constant for the reaction between 4-APZ and hydroxyl radicals was found to be $3.9 \pm 0.2 \times$

$10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. Complete mineralization could be attained with BDD anode, whereas Ti₄O₇ anode only showed excellent mineralization up to 94% TOC removal. Therefore, Ti₄O₇ anode can constitute a promising anode material thanks to its lower manufacturing cost. Inorganic ions like NO₃⁻ and HCO₃⁻ at concentration up to 25 mM has no effect on mineralization efficiency during AO-H₂O₂, but the presence of Cl⁻ even at lower concentration of 10 mM significantly reduced the TOC removal efficiency. The toxicity of the solution sharply increased at initial stage of treatment, corresponding to the formation of cyclic by-products but their conversion to carboxylic acids due to longer treatment time involved a sharp toxicity decrease, thus ensuring overall detoxification.

1. Introduction

The fate and remediation of pharmaceuticals and personal care products (PPCPs) as emerging pollutants in water and wastewater has become a relative issue in environmental research as well as of utmost concern for several health and environmental regulatory agencies in the last two decades.^[1,2] Several studies have recorded the presence of PPCPs from a wide spectrum of therapeutic classes in aquatic environment and ground water, which mainly enter via the municipal sewage treatment plants (STPs) effluents due to the inefficiency of the conventional water treatment technologies employed in most STPs.^[3-5] Despite natural attenuation processes

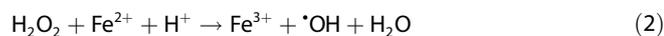
such dilution, partial (a)biotic degradation and sorption, PPCPs are found in concentration range from $\mu\text{g L}^{-1}$ in the effluent of STPs to ng L^{-1} in surface, ground and drinking water.^[1,2,6,7] Among the PPCPs, the occurrence of analgesics used in both human and veterinary medicine has received serious attention due to wide, large quantities and unrestricted use as well as concern for their negative effect in environment.^[8,9] 4-Aminophenazone (4-APZ) is an analgesic and antipyretic drug with annual consumption of 0.35 g per year and person in Germany between 1999–2006^[9] and has been found at $\mu\text{g L}^{-1}$ in sewage and surface water as well as raw water for production of drinking water.^[10-12] The ecotoxicity of 4-APZ is still largely unknown^[13] but ranks among the most relevant PPCPs for invertebrates and algae based on its typical environmental concentration and persistence.^[16]

Electrochemical advanced oxidation processes (EAOPs) are one of the most versatile and efficient technique for efficient removal of persistent organic pollutants including PPCPs due to their high versatility and environmental compatibility.^[15-18] Among EAOPs, anodic oxidation (AO) and electro-Fenton (EF) processes have been the most widely studied due to their ability to generate large quantities of strong oxidants which can completely mineralize any class of organics pollutants and their byproducts with high energy efficiency.^[19-21] In AO using high O₂ evolution overvoltage anodes, weakly sorbed hydroxyl radicals (M[•]OH) are generated via water oxidation (Eq. (1)) at the surface of anodes (M).^[22-24] Besides, when cathodes such carbon felt or gas diffusion cathodes are utilized, weak oxidant H₂O₂ is generated in large quantities and the process is termed AO-H₂O₂.^[25,26]

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On the other hand, *OH are produced in EF electrocatalytically via Fenton's reaction (Eq. (2)) between H_2O_2 electrogenerated at the cathode from dissolved oxygen (Eq. (3)) and Fe^{2+} added in catalytic quantity to the solution prior electrolysis.^[15,17,27-29] Interestingly, Fe^{2+} is continuously regenerated at the cathode by 1-electron reduction (Eq. (4)) of Fe^{3+} produced in Fenton reaction (Eq. (1)).^[30-33]



The efficiency of EF is greatly enhanced when anode materials with high overpotential for oxygen evolution such as BDD or Ti_4O_7 anode are used because of the large production of $M(^*OH)$ at the surface of the anode (Eq. (1)).^[33-36] This constitutes a significant advantage for process efficiency and operation cost and as such, make EF most exciting process compared to other AOPs such as Fenton and photo-Fenton processes.^[17,37] Indeed, BDD thin-film electrode remains the best known anode material for AO and Fenton's based EAOPs due to its high chemical stability and capacity to generate large quantities of stable physisorbed BDD (*OH) radicals which can completely mineralize any class of organic pollutants.^[15,17,18,20] However, sub-stoichiometric titanium oxides especially Ti_4O_7 has been recently proposed as alternative low cost electrodes for both AO and EF processes.^[34,38-41] It is considered significantly less expensive option compared to BDD because it is solely prepared from TiO_2 which is one of the cheapest feedstock on earth and has easy production route.^[42,43] But the quantity of $Ti_4O_7(^*OH)$ generated on this electrode is usually lower compared to BDD(*OH) produced on BDD of similar geometry at given experimental conditions, thus exhibiting slightly lower oxidation power compared to BDD electrode.^[38,43]

Several studies have reported the effectiveness of AO and EF for the complete removal of PPCPs from aqueous solutions and many of these studies have been summarized in several review papers.^[8,15,17,19,44,45] However, studies on electrochemical degradation of antipyretic drug 4-APZ have not been reported in literature. Therefore, this study reports, the degradation of antipyretic drug 4-APZ by AO- H_2O_2 and EF using BDD or Ti_4O_7 anode and carbon-felt cathode was investigated. The mineralization power of these two outstanding anodes were comparatively examined. The influence of applied current, initial concentration of 4-APZ and the presence of inorganic ions on the degradation kinetics and mineralization of the 4-APZ solutions were carefully studied. The evolution of generated carboxylic acids as well as inorganic ions released into the treated solution during electrolysis was followed by chromatography analysis. The evolution of the toxicity of the treated solution during electrolysis was followed by Microtox[®] method.^[38] The objective of this study was to determine the most suitable treatment strategy for the removal of 4-APZ by EAOPs.

2. Results and Discussion

2.1. Degradation Kinetics of 4-APZ

The decay of the concentration of 4-APZ over electrolysis time during AO- H_2O_2 and EF treatments of 0.192 mM 4-APZ solution (44.4 mg L⁻¹) at different applied currents using either BDD or Ti_4O_7 anode was followed by reversed phase HPLC, which always displays a well-defined symmetric peak at retention time (t_R) of 8.5 min (with detection limit of 10⁻⁵ M). Figure 1 shows the decay of the 4-APZ concentrations over time. Firstly, it is important to state that carbon-felt cathode has no sorption effect on 4-APZ. A fast and complete decay of 4-APZ concentration was observed in all trials, although shorter times were required for total destruction of initial 4-APZ molecules in EF treatment compared to AO- H_2O_2 as well as at higher applied current. The faster degradation observed during EF compared to AO- H_2O_2 could be explained by the large production of homogeneous *OH in the bulk solution from Fenton's reaction (Eq. (2)) in addition to the physisorbed $M(^*OH)$ generated at the anode surface (Eq. (1)), which can quickly oxidize the pollutants. Besides, the physisorbed $M(^*OH)$ was produced and confined to anode region only in AO- H_2O_2 , whereas homogeneous *OH was generated in the bulk of the solution in EF, thus EF process allows significant reduction of mass transport limitations commonly encounter in electrode processes at a given current values.^[25,47] Regarding the faster degradation of 4-APZ observed at higher current, this is expected because increased current accelerates both *OH and $M(^*OH)$ production from Fenton's reaction and water oxidation on the anode, respectively.^[30,32,46]

Thus, complete 4-APZ degradation was attained in 120, 60, 40 and 20 min for trials performed at 30, 60, 120 and 250 mA respectively during EF treatment using either BDD or Ti_4O_7 anode, whereas longer working time of 240, 120, 60 and 40 min were required for complete oxidation of 4-APZ at similar applied currents with either anode material during AO- H_2O_2 treatment. As can be seen in Figure 1, the performance of plasma elaborated Ti_4O_7 for the oxidative degradation of 4-APZ was quiet similar to that of BDD anode at a given experimental conditions, which is in agreement with our previous reports on electrochemical treatment of other pharmaceuticals.^[33,34,38]

The effect of initial 4-APZ concentration on its degradation trend at 120 mA using BDD anode, tailored at testing the oxidation ability of EF system for a range of organic matter content was shown in Figure 2a. A more rapid destruction of 4-APZ molecules was obtained for the treatment of 0.092 mM solution (22.2 mg L⁻¹), with total disappearance attained only in 10 min, compared to 40 min required during the treatment of 0.192 mM 4-APZ solution (44.4 mg L⁻¹). In contrast, a longer working time (60 min) was needed for total destruction of a higher concentration of 0.384 mM 4-APZ (88.8 mg L⁻¹) solution at similar experimental conditions. The longer working time required as the initial 4-APZ concentration increases was due to the presence of large quantities of 4-APZ molecules which reduces the hydroxyl radicals-pollutants ratio, and in turn the 4-APZ degradation rate. Besides, more organic intermediates formation are expected at higher initial concentration, thus reducing the 4-APZ degradation

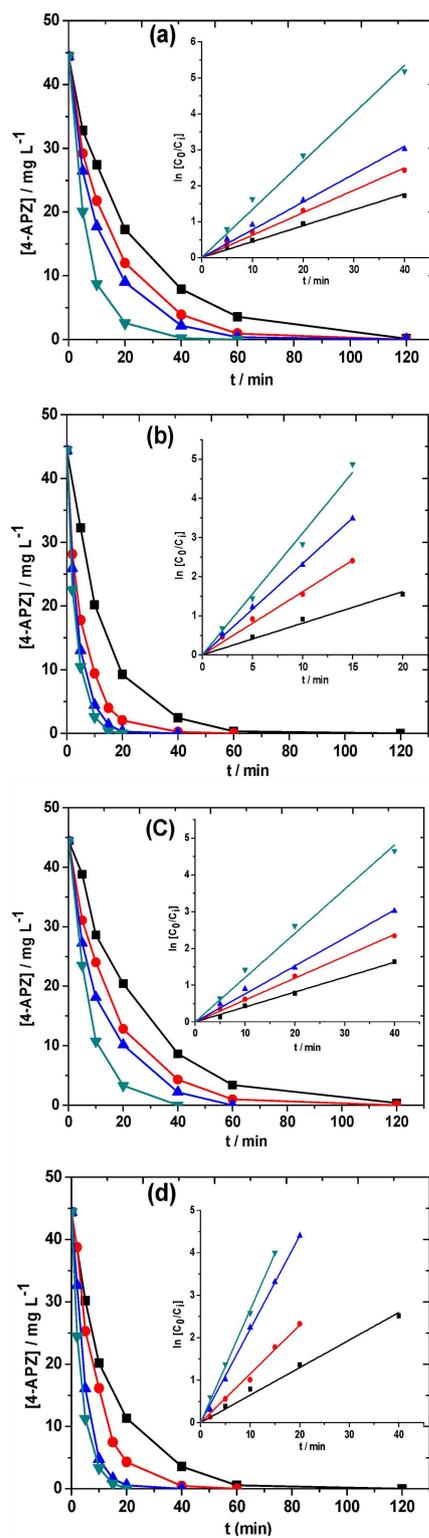


Figure 1. Decay of 4-APZ concentration vs electrolysis time for the (a, c) AO-H₂O₂ and (b, d) EF (0.2 mM Fe²⁺) treatments of 0.192 mM (44.4 mg L⁻¹) 4-APZ in 0.05 M Na₂SO₄ solutions at applied current of (■) 30 mA, (●) 60 mA, (▲) 120 mA and (▼) 250 mA using (a, b) BDD and (c, d) Ti₄O₇ anodes. The corresponding kinetic analyses assuming the oxidation of 4-APZ by [•]OH follows pseudo-first order kinetic are given in the inset panels.

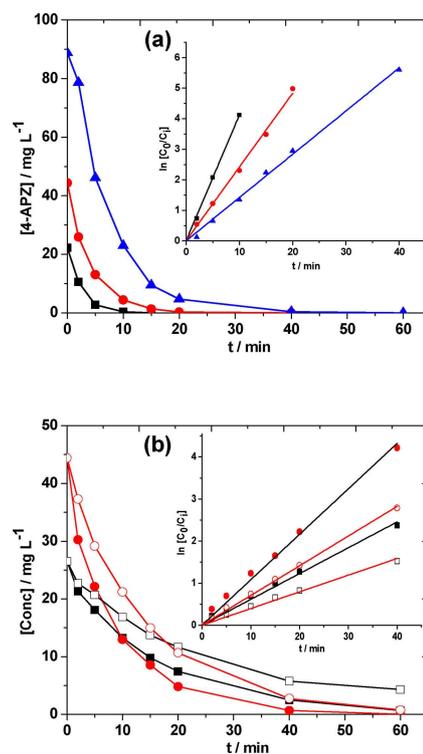


Figure 2. (a) Decay of 4-APZ concentration vs electrolysis time for the EF (0.2 mM Fe²⁺) treatment of (■) 0.096 mM, (●) 0.192 mM and (▲) 0.384 mM 4-APZ in 0.05 M Na₂SO₄ solution at applied current of 120 mA using BDD anode and (b) Decay of concentration of (●, ○) 4-APZ and (■, □) pHBA vs electrolysis time during EF treatment of the solutions containing 0.192 mM of each compound at applied current of (○, □) 60 mA and (●, ■) 120 mA using BDD anode. The corresponding kinetic analyses assuming the oxidation of 4-APZ and/or pHBA by [•]OH following pseudo-first order kinetic are given in the inset panels.

rate since hydroxyl radicals are non-selective oxidants and react with the intermediates generated.^[38,47] The complete destruction of 4-APZ even at higher concentration demonstrates high potential of electrochemical oxidation with BDD anode for total decontamination of organic polluted wastewater.

The corresponding kinetic analyses were shown in the inset panel of Figure 1 and Figure 2. The decay of the 4-APZ concentration fitted well with pseudo-first order reaction between the hydroxyl radicals and 4-APZ molecules, with excellent correlation ($R^2 > 0.99$). This implies that fixed amount of hydroxyl radicals ($M^{\bullet}OH$ and $^{\bullet}OH$) always reacts with 4-APZ following pseudo-first order kinetics.^[47] As shown in Table 1, the

Table 1. $k_{app,4-APZ}$ (min ⁻¹) for the reaction between [•] OH and 4-APZ assuming pseudo-first order kinetics.						
$k_{App,4-APZ}/min^{-1}$	[4-APZ]	[Fe ²⁺]	30 mA	60 mA	120 mA	250 mA
Cell	0.096	0.2	-	-	0.412	-
BDD/CF	0.192	0.2	0.081	0.161	0.233	0.311
	0.192	-	0.044	0.062	0.077	0.148
Ti ₄ O ₇ /CF	0.384	0.2	-	-	0.142	-
	0.192	0.2	0.065	0.115	0.220	0.265
	0.192	-	0.041	0.059	0.075	0.132
-	-	-	-	-	-	-

analysis demonstrated a gradual increase in apparent rate constants ($k_{app(4-APZ)}$) values with rising in applied current from 30 to 250 mA for all the trials studied. As expected, the $k_{app(4-APZ)}$ values obtained during EF treatment were higher compared to AO- H_2O_2 at all currents studied for both anodes due to the large quantities of homogeneous $\cdot OH$ produced in the bulk, which accelerates the degradation of 4-APZ. Similar working times

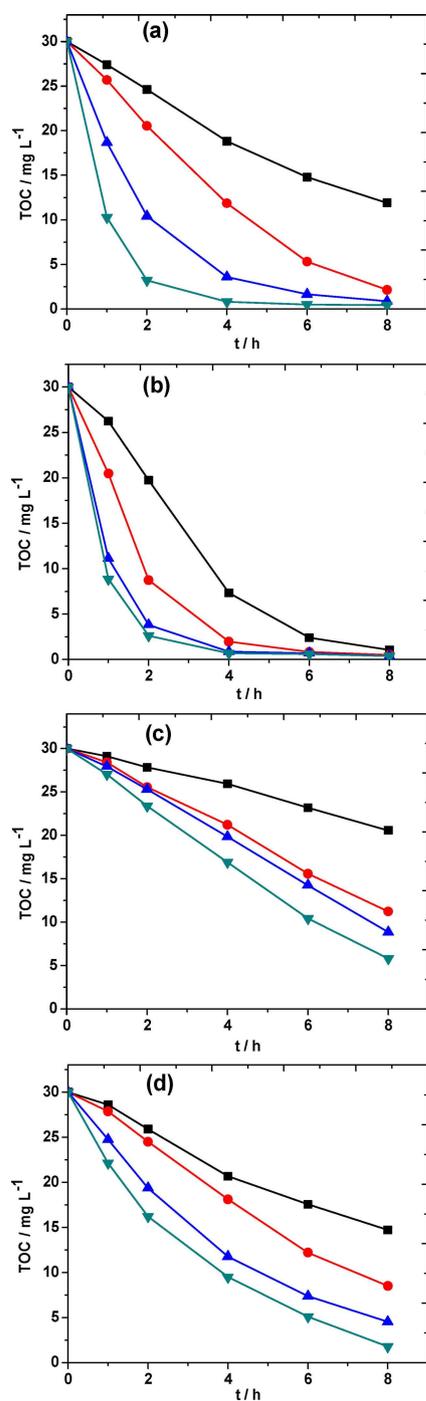


Figure 3. TOC decay vs electrolysis time for the mineralization of 4-APZ solution: (a, c) AO- H_2O_2 and (b, d) EF (0.2 mM Fe^{2+}) treatments of 0.192 mM (30 mg L^{-1} TOC) 4-APZ in $0.05 \text{ M Na}_2\text{SO}_4$ solution at applied current of (■) 30 mA, (●) 60 mA, (▲) 120 mA and (▼) 250 mA using (a, b) BDD and (c, d) Ti_4O_7 anodes.

were required at all current studies for the total disappearance of 4-APZ in EF or AO- H_2O_2 for both BDD and Ti_4O_7 anodes (Figure 1), but the $k_{app(4-APZ)}$ values (Table 1) showed that BDD anode has slightly higher degradation rate compared to Ti_4O_7 anode at similar experiment conditions, demonstrating the superior oxidation potential of BDD anode. It is important to note that, the rate constant did not increase proportionally with rising current, suggesting the progressive enhancement of parasitic reactions and possibility of the destruction rate reaching maximum at certain applied current value.^[30,34,47] As expected, the rate constant decreases with rising in initial concentration of 4-APZ as depicted in Table 1, owing to decreased 4-APZ molecules-hydroxyl radical ratio.

The second-order or absolute kinetic rate ($k_{abs(4-APZ)}$) for the reaction between 4-APZ and $\cdot OH$ was determined by competition kinetics method, using pHBA as standard competition substrate with a well-known absolute rate constant ($k_{abs(pHBA)} = 2.19 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).^[48] EF experiments were conducted using solution containing equimolar concentrations of pHBA and 4-APZ at pH 3 and applied current of 60 and 120 mA using BDD anode. The analyses of electrolyzed solutions using reversed phased HPLC showed two peaks at 4.2 and 8.5 min, corresponding to p-HBA and 4-APZ respectively. The decay of the concentration of both compounds decreased exponentially (Figure 2b), in agreement with pseudo-first order kinetics and the k_{app} values ($R^2 > 0.99$) obtained from the slopes in inset panel of Figure 2b were 0.040 and 0.071 min^{-1} at 60 mA and 0.061 and 0.108 min^{-1} at 120 mA for pHBA and 4-APZ, respectively. Using this data and relationship in Eq. (5),¹⁷ $k_{abs(4-APZ)}$ values of 3.92×10^9 and $3.88 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ were obtained at 60 and 120 mA respectively, which gave an average value of $3.87 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value was quite similar to others reported for oxidative degradation of pharmaceuticals with $\cdot OH$ ($3.36 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)^[47] and $3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ^[33] for propranolol and $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for tetracycline).^[49]

$$k_{abs(4-APZ)} = k_{abs(pHBA)} \left[\frac{k_{app(4-APZ)}}{k_{app(pHBA)}} \right] \quad (5)$$

2.2. Mineralization of 4-APZ

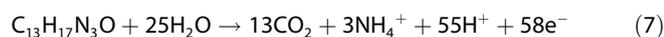
The excellent efficacy of AO- H_2O_2 and EF treatments with either BDD or Ti_4O_7 anode for complete destruction of acidic 4-APZ solutions has been demonstrated. It is important to note that the degradation of organic pollutants by AOPs/EAOPs results in the formation of numerous by-products, which are also attacked by the hydroxyl radicals, thus it is necessary to verify the potential of the applied EAOPs for total removal of all oxidizable organics from the aqueous solution. Figure 3 showed TOC decays vs electrolysis time for the mineralization of 4-APZ solutions obtained at similar operating conditions as in Figure 1. In all the four cases, the TOC removal rate increases with rise in applied current. For instance, during the AO- H_2O_2 treatment with BDD and Ti_4O_7 anodes (Figure 3a and 3c), TOC removal of 60, 93, 97 and 98% and 32, 63, 71, and 82% were achieved after 8 h of electrolysis at 30, 60, 120 and 250 mA for BDD and Ti_4O_7 anodes, respectively. Similar trend

was observed for EF treatments (Figure 3b and 3d) but with enhanced mineralization efficiency especially with Ti_4O_7 anode. The TOC removal efficiency of 96, 97, 98 and 99% and 51, 72, 85 and 94% were attained at applied current of 30, 60, 120 and 250 mA for BDD and Ti_4O_7 anodes, respectively. As explained in section 2.1, the enhanced mineralization with rising applied current was expected owing to the greater amount of $\text{M}(\cdot\text{OH})$ ($\text{AO-H}_2\text{O}_2$) and $\cdot\text{OH}$ (EF) produced from water oxidation and Fenton's reaction, which can accelerate the mineralization of both 4-APZ and its organic intermediates. It is noteworthy that the enhancement observed when increasing the applied current from 30 to 120 mA (lower current) was more remarkable compared to when raising the current from 120 to 250 mA especially during treatments with BDD anode, which suggesting that the oxidation rate is determined by mass transports of substances (i.e. O_2 , 4-APZ and its intermediates and/or Fe^{2+}) towards the electrodes at higher applied current.^[30,47] Again, rapid and improved TOC decay was achieved with EF (Figure 3b and 3d) compared to $\text{AO-H}_2\text{O}_2$ (Figure 3a and 3c) treatments because EF allows production of high amount of $\cdot\text{OH}$ in the bulk and the fact that the oxidizing species are not confined to the electrode surface or its vicinity allows the easier interaction between the $\cdot\text{OH}$ and organic molecules within the entire bulk solution.^[15,47] Additionally, treatments with BDD anode (Figure 3a and 3b) showed faster and excellent mineralization compared to Ti_4O_7 anode (Figure 3c and 3d) at all current studied, demonstrating the higher potential of BDD anode for generation of large quantities of physisorbed radical (BDD($\cdot\text{OH}$)) compared to Ti_4O_7 anode at similar experimental conditions. Both BDD and Ti_4O_7 anodes are considered "non-active anode" but previous studies have shown that the quantity of physisorbed radical produced at the surface of BDD anode is higher compared to Ti_4O_7 anode.^[38,43]

The corresponding mineralization current efficiency (MCE) for the trials of Figure 3, estimated according to Eq. (6) are shown in Figure 4.

$$\text{MCE} (\%) = \frac{(\Delta\text{TOC})_{\text{exp}} n F V_s}{4.32 \times 10^7 m I t} \times 100 \quad (6)$$

where F is the Faraday constant (96487 C mol^{-1}), V_s is the solution volume (L), 4.32×10^7 is a conversion factor ($= 3,600 \text{ s h}^{-1} \times 12,000 \text{ mg of C mol}^{-1}$), m is the number of carbon atoms of 4-APZ (13 C atoms), I is the applied current (A) and n is the number of electrons consumed per molecule of 4-APZ; taken to be 58 assuming complete mineralization of 4-APZ into CO_2 , NH_4^+ and H_2O according to Eq. (7).



Higher efficiency was obtained with BDD anode (Figure 4a and 4b) compared to Ti_4O_7 anode (Figure 4c and 4d) as well as EF treatments (Figure 4b and 4d) compared to $\text{AO-H}_2\text{O}_2$ (Figure 4a and 4c). Also, a lower applied current led to a higher MCE at any time for all trials, which indicates that the hydroxyl radicals were used more efficiently in the oxidation of organic molecules, even though the $\cdot\text{OH}$ concentration generated was

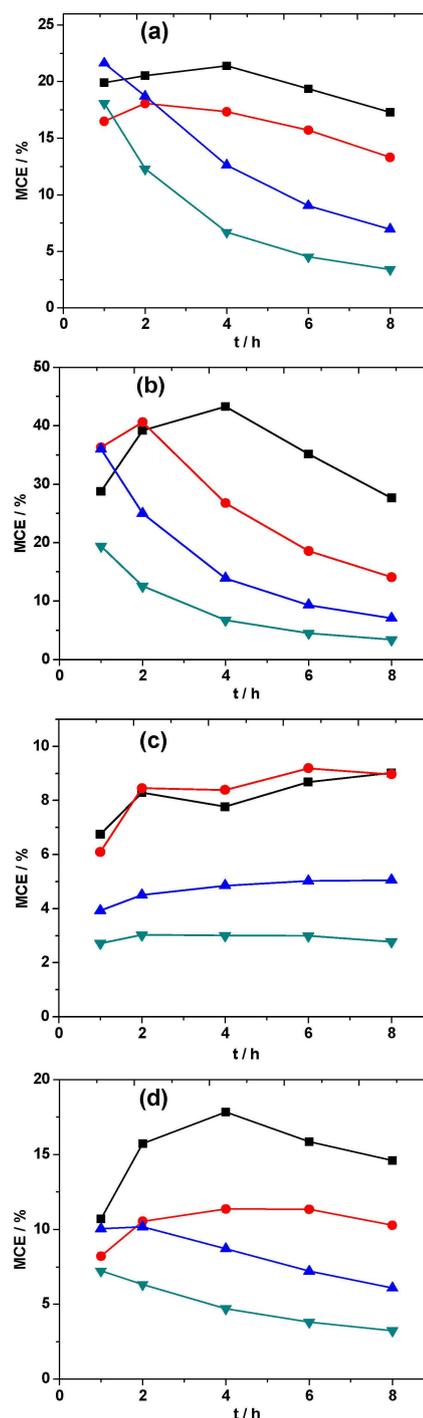


Figure 4. Evolution of MCE% vs electrolysis time and current corresponding to the treatments shown in Figure 3a–3d.

lower. Regardless of the process and the anode materials used, the MCE always underwent progressive decay over time and applied current, which can be explained by: (i) the depletion of the concentration of organic matter in the solution which may result in increasing mass transport limitation, (ii) formation of more refractory by-products which are less oxidizable by hydroxyl radicals and (iii) gradual loss in relative quantity of $\cdot\text{OH}/\text{M}(\cdot\text{OH})$ available in the solution owing to the

enhancement of waste reactions competing with oxidation of organic matter.^[30,34,47] The waste reactions include “self-destruction and dimerization” of the radical as well as reaction between $\cdot\text{OH}$ and Fe^{2+} and/or H_2O_2 .^[33,38] Moreover, $\text{MCE} < 100\%$ was observed in all case, which indicates energy loss attributed to that fact that $\cdot\text{OH}/\text{M}(\cdot\text{OH})$ production requires mass transport of reactants and organics as well as current expended on H_2 evolution at the cathode in acid medium.^[23]

The effect of initial 4-APZ solution concentrations on TOC decay was studied by comparatively treating solution containing 0.096 mM, 0.192 mM and 0.384 mM (i.e. 15, 30 and 60 mg L⁻¹ TOC) by EF (0.2 mM Fe^{2+}) process at 120 mA using BDD anode. As shown in Figure 5a, quite similar mineralization rates (TOC removal kinetics) were observed at all the initial concentration studied. This is an appealing characteristic, which implies that the EF process can efficiently operate well with relatively high organic content. Moreover at high pollutant concentration, parasitic reactions that waste/consume the hydroxyl radicals are minimized because the oxidizing species interact with a large number of molecules that were available in the bulk. This resulted in a large amount of TOC being removed when treating 0.384 mM 4-APZ solution as shown in the inset panel of Figure 5a. As such, a more efficient process (high MCE) was observed when treating a solution containing higher organic matter as shown in Figure 5b. In fact, the MCE

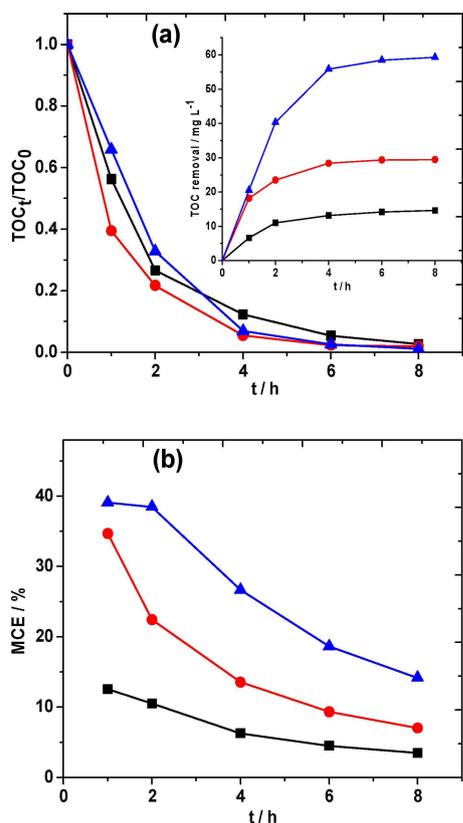


Figure 5. Effect of initial 4-APZ solution concentration: (■) 0.096 mM (15 mg L⁻¹ TOC), (●) 0.192 mM (30 mg L⁻¹ TOC) and (▲) 0.384 mM (60 mg L⁻¹ TOC) on the (a) TOC decay vs electrolysis time and (b) MCE vs electrolysis time during the EF (0.2 mM Fe^{2+}) treatment using BDD anode at 120 mA and pH 3. The amount of TOC removal vs electrolysis time is shown in the inset panel of (a).

increases with rise in initial 4-APZ concentrations, thus attaining maximum of 13%, 35% and 39% for 0.096 mM, 0.192 mM and 0.384 mM 4-APZ solution respectively, at the studied experimental conditions.

The influence of the presence of other inorganic ions such HCO_3^- , NO_3^- and Cl^- in the treated solution on the TOC decay during the AO- H_2O_2 using BDD anode was investigated and reported in Figure 6. In general, real wastewater or STPs effluents are usually multi-components, contain several inorganic ions in various concentration levels as well as natural organic matters. As depicted in Figure 6, NO_3^- and HCO_3^- at concentration studied (10 mM and 25 mM, the concentration range found in reverse osmosis concentrate)^[50] has no significant effect on the TOC decay of 4-APZ solution. However, the presence of 10 mM Cl^- ions reduced the mineralization efficiency of 4-APZ solution during the AO- H_2O_2 treatment. The TOC decay rate was further reduced when the concentration of Cl^- ions was raised to 25 mM (Figure 6b). Similar observations have previously been reported during the degradation of *N*-nitrosodimethylamine (NDMA) in reverse osmosis concentrate.^[50] The authors showed that NDMA oxidation rate was not affected by the dissolved organic carbon or HCO_3^- at concentration present in osmosis concentrate, however, hydroxyl radicals scavenging occurs at 100 mM concentration of Cl^- or HCO_3^- , which retarded the oxidation of NDMA. In the case of Cl^- medium, other studies have attributed the reduction in

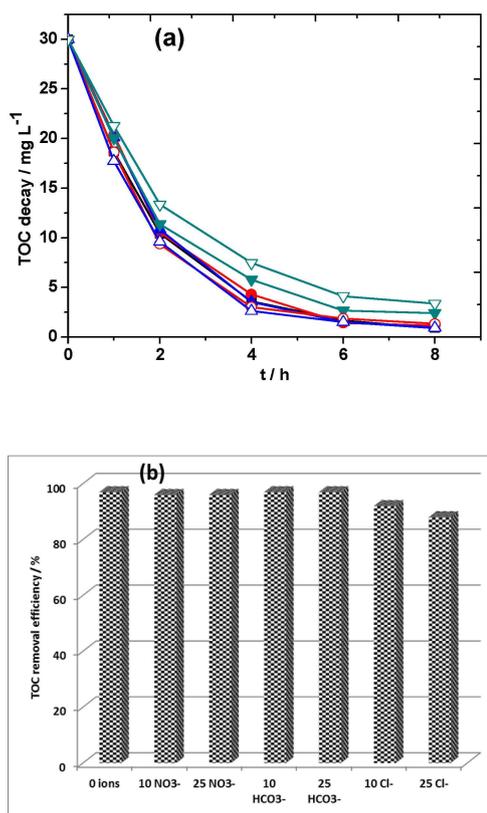


Figure 6. (a) Effect of the presence of inorganic ions: (●, ○) NO_3^- , (▲, △) HCO_3^- and (▼, ▽) Cl^- at concentration of (■) 0 mM, (●, ▲, ▼,) 10 mM and (○, △, ▽) 25 mM on the TOC decay vs electrolysis time during the AO- H_2O_2 treatment of 0.192 mM (30 mg L⁻¹ TOC) 4-APZ 0.05 M Na_2SO_4 solution using BDD anode at 120 mA. (b) The corresponding TOC removal efficiency.

mineralization efficiency to the formation of highly refractory chloro-organics which are less oxidizable by hydroxyl radicals.^[26,51]

2.3. Evolution of Oxidation Intermediates

Oxidative destruction of organic pollutants by hydroxyl radicals usually lead to the formation of aromatic/cyclic intermediates as the main primary by-products, which are further degraded to short-chain carboxylic acids as the final organic by-products before complete mineralization with the release of inorganic ions. The detection of inorganic ions in the final solution constitutes another evidence, along with TOC removal results, of the mineralization of the organic pollutants whereas, the presence of carboxylic acids account for the remnant/residual TOC in the final solution after treatments.^[52,53] Ion-exclusion chromatography analyses of the solutions treated by EF process using either BDD or Ti_4O_7 anode at pre-selected time always showed chromatograms with six well displayed peaks at 6.8, 8.9, 10.1, 12.5, 14.4 and 17.8 min corresponding to oxalic, maleic, malic, oxamic, glyoxylic and acetic acids. These acids were confirmed by injecting their standard solutions using ion-exclusion HPLC. In all trials, the concentration profile of all the acids detected displayed accumulation-destruction-cycles with their formation started right from the beginning of the electrolysis (Figure 7a and 7b). The accumulations of the acids came from the cleavage and degradation of 4-APZ and its cyclic/aromatic by-products at the early stage of treatment but were then degraded with longer treatment time by the large quantities of hydroxyl radicals generated at the anode surface as well as in bulk. Oxalic and glyoxylic acids showed the largest accumulation and higher persistence (Figure 7), which suggests that they can be formed from both cleavage of 4-APZ and its cyclic intermediates as well as from further degradation of higher molecular carboxylic acids like maleic and malic acids. Interestingly, all the acids were efficiently mineralized during EF with BDD (Figure 7a) anode compared to Ti_4O_7 anode (Figure 7a), in agreement with the complete mineralization degree and excellent TOC decay reported in Figure 3b and Figure 3d respectively.

The release of the initial nitrogen content of 4-APZ to the solution in the form of inorganic ions such as NH_4^+ , NO_3^- , and NO_2^- was monitored by ion chromatography during the mineralization of 0.192 mM of its solutions (corresponding to 0.576 mM initial nitrogen) by EF process using either BDD or Ti_4O_7 anode at 120 mA. No nitrite ions were detected by the chromatographic analyses. As depicted in Figure 7c and 7d, the inorganic ions were formed from the beginning of the treatment, meaning that the mineralization of the pollutants starts simultaneously as the current was applied. The NH_4^+ ions were predominant, in agreement with the complete mineralization of 4-APZ solution according to Eq. (7). A rapid accumulation of both NH_4^+ and NO_3^- ions was observed at the early stage of treatment, in agreement with fast destruction of 4-APZ and TOC decay. After 8 h of EF treatment, the concentration of NH_4^+ attained 0.37 mM (64% of initial N) and 0.33 mM (58% of initial N) for the treatment with BDD and Ti_4O_7 anodes, respectively, whereas 0.18 mM (31% of initial N) and 0.18 mM (31% of initial N) were the final

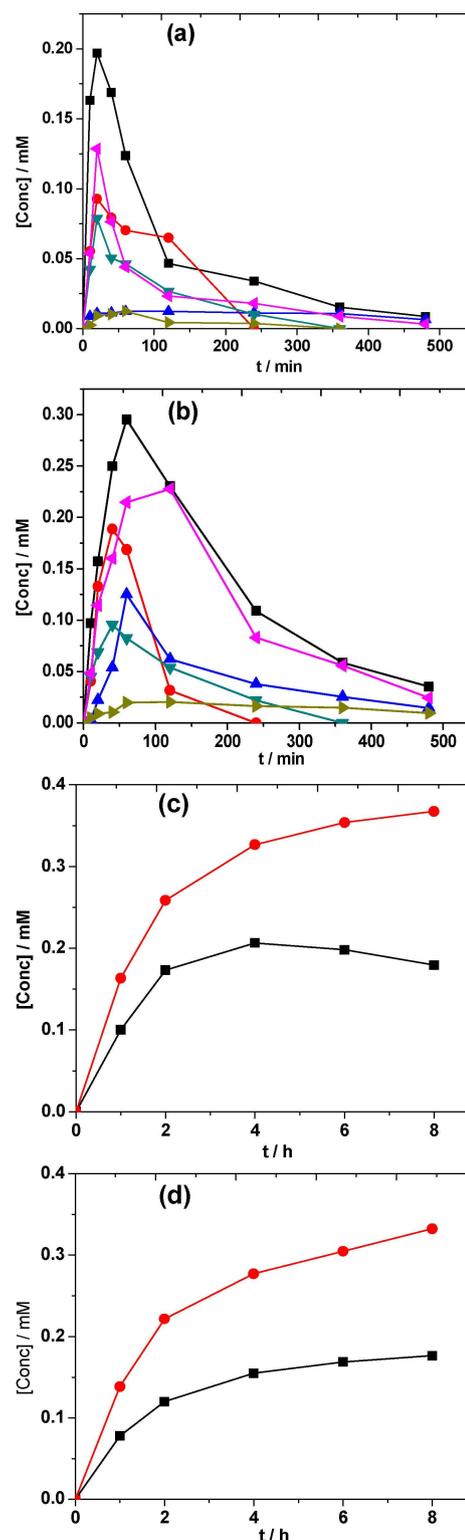


Figure 7. Evolution of concentration of formed (a, b) carboxylic acid: (■) oxalic, (●) Maleic, (▲) oxamic, (▼) malic, (◀) glyoxylic and (▶) acetic acids; and (c, d) inorganic ions: (●) NH_4^+ and (■) NO_3^- vs electrolysis time during the EF (0.2 mM Fe^{2+}) treatment of 0.192 mM (30 mg L^{-1} TOC) 4-APZ in $0.05 \text{ M Na}_2\text{SO}_4$ solution using (a,c) BDD and (b,d) Ti_4O_7 anodes at 120 mA and pH 3.

concentration of NO_3^- found in the EF treated solutions with BDD and Ti_4O_7 anodes respectively. The total nitrogen found in the final treated solutions was 0.55 mM (95% of initial N) and 0.51 mM (89% of initial N) for BDD and Ti_4O_7 anodes respectively, demonstrating relatively higher mineralization power of BDD anode compared to Ti_4O_7 anode. This implies that there were some refractory nitrogenous compounds mostly oxamic acid (0.017 mM) remaining in the treated solutions especially when Ti_4O_7 anode was utilized as depicted in Figure 7b. Further, some of the initial nitrogen atom may have also been lost as volatile N_xO_y compounds as previously reported by Garcia-Segura et al (2017)^[54] and others^[55,56] using in-situ differential mass spectroscopy.

2.4. Assessment of Acute Toxicity

The evolution of toxicity of the treated solutions containing 0.192 mM 4-APZ over electrolysis time was studied using EF treatments with either BDD or Ti_4O_7 anode at applied current of 120 mA using Microtox[®] test based on the *V. fischeri* bacteria luminescence inhibition caused by the presence of 4-APZ and its oxidation intermediates. As shown in Figure 8, the two experimental curve profiles corresponding to the percentage inhibitions, demonstrated similar features. In both cases, a strong initial rise in luminescence inhibition percentage was observed, indicating a considerably higher toxicity of the primary 4-APZ intermediate

products. Previous studies have shown that formation of cyclic compounds/intermediates is predominantly in the first stage of electro-Fenton process, which are responsible for the maximum values of 99–100% inhibition attained.^[46] The maximum inhibition lasted for almost similar time in both cases, indicating that both 4-APZ and its cyclic intermediates were destroyed at almost similar rate with either BDD or Ti_4O_7 anode and the difference in TOC decay was majorly due to mineralization of refractory short-chain carboxylic acids, which are degraded faster with BDD anode compared to Ti_4O_7 anode. This was immediately followed by sharp decrease in percentage inhibition, suggesting the toxicity decay, and sudden increase from 60 min for both cases. The second maximum value of the percentage inhibition, which is lower than the first maximum (higher for Ti_4O_7 anode compared to BDD) but still higher than the percentage inhibition of initial 4-APZ solution, was attributed to the formation of secondary intermediates which are less toxic compared to primary oxidation by-products. Longer treatment time causes toxicity decay again and, after 240 min, the percentage inhibition reached its minimum value, which can be explained by the destruction of 4-APZ and its cyclic by-products into short-chain carboxylic acids that are found in the final treatment solutions and exerted very low toxicity toward *V. fischeri*.

3. Conclusions

Complete degradation and excellent mineralization of acidic solution of 4-APZ has been achieved by AO- H_2O_2 and EF treatments using BDD or Ti_4O_7 anode and carbon-felt cathode. 4-APZ and its oxidation reaction intermediates were oxidized by $\cdot\text{OH}$ produced from Fenton's reaction between continuously electro-generated H_2O_2 and Fe^{2+} and/or physisorbed $\cdot\text{OH}$ produced at the BDD/ Ti_4O_7 anode surface. Total mineralization (TOC removal >99%) could be attained with BDD anode in either EF or AO- H_2O_2 , demonstrating the efficacy of electrochemical treatment with this electrode. In contrast, EF and AO- H_2O_2 with Ti_4O_7 at similar conditions provided also high mineralization rates of 94% and 82%, respectively, with the remnant TOC accumulated in the solution as short-chain carboxylic acids. Carboxylic acids being biodegradable, the solution can be further treated biologically when a total mineralization is needed.^[57] The TOC removal efficiency during AO- H_2O_2 was not affected with the presence of NO_3^- or HCO_3^- at concentration up to 25 mM, however it was significantly reduced in the presence of Cl^- . Kinetic analyses of 4-APZ decay always followed pseudo-first order kinetic reaction and higher rate constant values were attained with EF compared to AO- H_2O_2 as well as BDD compared Ti_4O_7 anode. Chromatographic analyses of the EF treated 4-APZ solutions showed the formation of short-chain carboxylic acids like oxalic, oxamic, maleic, malic and glyoxylic as the final organic by-products, with the initial nitrogen content released as NH_4^+ and NO_3^- ions. The initial 4-APZ solution showed relatively low luminescence inhibition to *V. Fischeri* bacteria, but sharply rised to maximum at early treatment stage and later reduced to minimum after longer treatment time. The AO- H_2O_2 and EF processes with BDD or Ti_4O_7 anode are efficient treatment techniques for complete degradation and

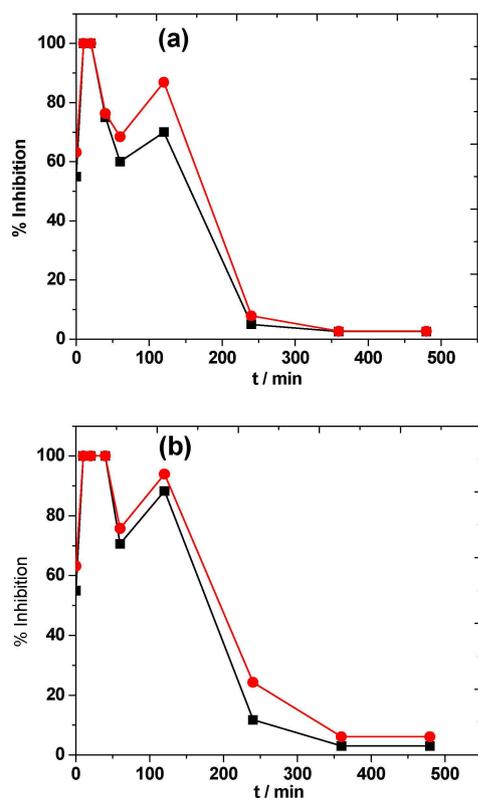


Figure 8. Evolution of percentage inhibition vs electrolysis time during the EF treatment of 0.192 mM (30 mg L⁻¹ TOC) 4-APZ in 0.05 M Na₂SO₄ solution using (a) BDD and (b) Ti_4O_7 anodes at 120 mA and pH 3 after (■) 5 and (●) 15 min exposure of samples to *V. fischeri*.

detoxification of 4-APZ solution. Finally, although Ti_4O_7 anode provides slightly lower performances compared to BDD, it remains an interesting alternative for a cost-effective process thanks to its lower manufacturing cost.

Experimental Sections

Chemicals

4-APZ ($\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}$) (Figure 9), sodium sulfate (Na_2SO_4), sodium nitrate (NaNO_3), sodium hydrogen carbonate (NaHCO_3), sodium chloride (NaCl), p-hydrobenzoic acid (p-HBA) and iron (II) sulfate heptahydrate were obtained from Sigma-Aldrich and used without further purification. Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) used to adjust solution pH were of analytical grade from Acros Organics and Fluka. Oxalic ($\text{H}_2\text{C}_2\text{O}_4$), oxamic ($\text{C}_2\text{H}_3\text{NO}_3$), acetic ($\text{C}_2\text{H}_4\text{O}_2$), maleic ($\text{C}_4\text{H}_4\text{O}_4$), glyoxylic ($\text{C}_2\text{H}_2\text{O}_3$) and malonic ($\text{C}_3\text{H}_4\text{O}_4$) acids used as standards for quantifying short-chain carboxylic acids generated during EF treatment were obtained from Acros, Fluka and Alfa Aesar. Bioluminescence bacteria and the activation reagent LCK 487 LUMISTOX were supplied by Hach Lange France SAS. All solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q system with resistivity $>18\text{ M}\Omega\text{ cm}$ at 25°C . Organic solvents and other chemicals used were either HPLC or analytic grade from Sigma-Aldrich, Fluka and Merck. All experiments were carried out in duplicate.

Electrochemical Cell

All electrolyses were performed in an open, cylindrical and undivided glass cell of 6 cm diameter and 250 mL capacity equipped with two electrodes and constantly stirred with PTFE magnetic bar to enhance mass transfer of substance towards/from the electrodes. The anode material was 24 cm^2 made of either Ti_4O_7 ($4\text{ cm}\times 6\text{ cm}$ thin film plasma deposited on Ti, Saint Gobain C.R. E.E., France) or BDD ($4\text{ cm}\times 6\text{ cm}$ thin film deposited on Nb support, Condis Gmbh, Germany), while the cathode was a tri-dimensional, large surface area carbon-felt (CF) ($14\text{ cm}\times 5\text{ cm}\times 0.5\text{ cm}$, Carbone-Lorraine, France).

The Ti_4O_7 anode was prepared following the procedure reported elsewhere.^[38] Briefly, TiO_x powder is produced by electrofusion of a mixture of TiO_2 and coke in an electrical arc-furnace. This powder is introduced into the plasma plume obtained by ionization of a mixture of argon and hydrogen in a torch. The high temperature reached in the plasma plume (10 000 to 15 000 $^\circ\text{C}$) leads to the melting of the TiO_x powder, which is accelerated onto a titanium substrate. A coating of typically 300–500 μm thickness is built layer by layer by the motion of the plasma torch; the mechanical anchorage of the coating on the metallic substrate is ensured by a preliminary sand-blasting of the substrate. Electrofusion is a widely

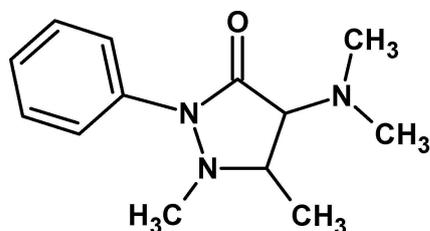


Figure 9. Chemical structure of 4-Amino-2, 3-dimethyl-1-phenyl-3-pyrazolin-5-one, Amprone (4-aminophenazone/4-aminoantipyrine).

used technology (mainly for abrasives and refractories industries) that makes it possible to produce hundreds of kilograms of powder; plasma spraying is also a very common technology that enables the production of coatings up to several square meters. Large TiO_x anodes can thus be produced by relatively cheap and industrially mature technologies.

The anode was always centred in the electrolytic cell, surrounded by the CF cathode and compressed air was continuously bubbled into the cell at about 1 L min^{-1} , starting 10 min before the electrolysis to reach a stationary O_2 concentration level in the solution. Except otherwise stated, all the trials were performed with 230 mL aqueous solutions of 0.192 mM (30 mg L^{-1} TOC) containing 0.05 M Na_2SO_4 as supporting electrolyte with 0.2 mM Fe^{2+} as electrocatalysts (EF) or without Fe^{2+} (AO- H_2O_2) at pH 3 and constant applied current in the range of 30–250 mA. The influence of inorganic ions was studied by adding 10 mM or 25 mM of Cl^- , HCO_3^- or NO_3^- to the treated solution. All trials were conducted at room temperature ($23\pm 2^\circ\text{C}$) and pH 3.

Analytical Procedure

Solutions pH was measured by a CyberScan pH 1500 pH-meter (Eutech Instruments). All electrolyses were performed with a Hameg HM8040 triple power supply at a constant current. The mineralization of the treated 4-APZ solutions were analyzed from the decay of the dissolved organic carbon, which can be considered as the total organic carbon (TOC) in the case of highly water-soluble organic compounds like 4-APZ. A Shimadzu VCSH TOC analyzer was used to measure TOC in accordance with the thermal catalytic oxidation principle. Reproducible TOC values, within $\pm 2\%$ accuracy were found using the non-purgeable organic carbon method.

Time course of 4-APZ concentration during its degradation was followed by reversed phase HPLC using a Merck Lachrom liquid chromatograph, equipped with a L-7100 pump, fitted with a Purospher RP-18, 5 μm , $25\text{ cm}\times 4.6\text{ mm}$ (i.d.) column at 40°C and a L-7455 photodiode array detector selected at the wavelength of 254 nm. 20 μL aliquots were injected into the HPLC setup with isocratic elution of the column by a mixture of methanol/acetate buffer at 60:40 (v/v) as the mobile phase at 0.8 mL min^{-1} flow rate. The identification and quantification of generated carboxylic acids was followed by ion-exclusion HPLC using Merck Lachrom liquid chromatograph equipped with a L-2130 pump, fitted with a 30-cm Supelcogel H column ($\phi\ 7.8\text{ mm}$) at 40°C , and coupled with a L-2400 UV detector selected at wavelength of 210 nm, using 1% H_2SO_4 at 0.2 mL min^{-1} as mobile phase. Inorganic ions majorly NH_4^+ and NO_3^- released in the treated solutions were analyzed by an ion-chromatography (ICS-1000, Dionex) coupled with a Dionex DS6 conductivity detector. A Dionex CS12A, $25\text{ cm}\times 4\text{ mm}$ (i.d.) cation column was used to quantified the NH_4^+ content using 9 mM H_2SO_4 as mobile phase at a flow rate of 1.0 mL min^{-1} , whereas NO_3^- concentration was quantified by a Dionex AS4A-SC, $25\text{ cm}\times 4\text{ mm}$ (i.d.) anion-exchange column eluted with a mixture of 1.8 mM Na_2CO_3 and 1.7 mM NaHCO_3 solution at 2.0 mL min^{-1} as mobile phase.

The toxicity of 4-APZ solution during EF treatment was monitored by Microtox[®] method [43,49]. Measurements were based on the inhibition of the bio-luminescence of the bacteria *V. fischeri* using a Mictox[®] analyzer. Prior to Microtox[®] analysis, the pH of all the samples was adjusted to 6.5–7.5 with the aid of 0.01–0.1 mM NaOH solution. The bioluminescence measurements were performed on both blank as well as electrolyzed solutions initially containing 4-APZ. In all cases, the bioluminescence intensity of *V. fischeri* bacteria were measured after 5 and 15 min of exposition to the sample at 15°C .

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Anodic oxidation · Electro-Fenton · 4-aminophenazone · Boron-doped diamond · Sub-stoichiometric titanium oxide (Ti₄O₇)

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