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ELECTROCHEMICAL MINERALIZATION OF ROTENONE AND PARAQUAT PESTICIDES USING BORON-DOPED DIAMOND ANODE. ELUCIDATION OF THE KEY ROLE OF DISSOLVED OXYGEN

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ABSTRACT: The degradation of the two pesticides rotenone and paraquat by anodic oxidation using a boron doped diamond (BDD) anode and a carbon felt cathode were studied. The effects of various operating parameters (dissolved oxygen, nature of electrolyte and applied current) on the degradation rate and the mineralization efficiency have been investigated and the key-role of dissolved oxygen elucidated. A very high mineralization rates were obtained for both pesticides (yielding 98% and 97% COD and TOC decay, respectively). The decay kinetics follow a pseudo-first order reactions. Reversed-phase chromatographic analysis revealed the appearance of various aromatic intermediates. Among them, hydroquinone and 12aβ-hydroxyrotenone which were identified by LC-MS-MS as oxidative degradation by-products of rotenone. The mineralization effectiveness was exhibited following the concentration profiles of generated short-chain aliphatic carboxylic acids (such as formic, oxalic, acetic and succinic acids) using ion-exclusion chromatography. The mineralization process of paraquat leads to a complete release of nitrate ions and to the total disappearance of chloride ions at the end of treatment.

Keywords: Anodic oxidation, BDD anode, dissolved oxygen, rotenone, paraquat.

RÉSUMÉ : L'étude développée au cours de ce travail a pour objectif de montrer que l'oxydation anodique sur électrode de DDB est une technique qui permet la dégradation et la minéralisation quasi-totale de deux pesticides : la rotenone et le paraquat. L'étude de l'effet de certains paramètres expérimentaux (oxygène dissous, nature de l'électrolyte et intensité du courant appliqué) a permis d'améliorer de façon significative l'efficacité du traitement et de définir les conditions adéquates pour la dégradation effective des deux pesticides. Un rôle-clé de l'oxygène dissous a été élucidé. Des taux de minéralisation très élevés ont été obtenus pour les deux pesticides (98% pour la roténone et 97% pour le paraquat). L'étude cinétique montre que la réaction d'hydroxylation est de pseudo-premier ordre pour les deux composés. Les analyses chromatographiques ont montré l'apparition d'intermédiaires réactionnels aromatiques. L'oxydation intensive des ces derniers conduits à la formation d'acides carboxyliques (les acides : acétique, formique, oxalique et succinique) qui ont été identifié par chromatographie. Le processus de minéralisation du paraquat conduit à une libération totale des ions nitrates et une disparition complète des ions chlorures à la fin du traitement.

Mots clés: oxydation anodique, anode DDB, oxygène dissous, rotenone, paraquat.

INTRODUCTION

Over the last few years, a large variety of powerful oxidative and environmentally friendly methods for water decontamination have been developed with the aim of avoiding dangerous impact of persistent organic pollutants that accumulate on the ecosystem and human health.

Many papers reported the use of several advanced oxidation processes (AOP's) for the

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treatment of toxic organics in water [1-15]. These techniques are based on the intermediacy of highly reactive chemical oxidants such as hydroxyl radicals to oxidize a wide range of refractory organic contaminants to various by-products and then lead to their mineralization into carbon dioxide, water and inorganic ions.

One of the most promising AOP's is the anodic oxidation method (AO), based on the oxidation of organics by either direct electron transfer reaction from pollutants to the electrode surface or the production of adsorbed •OH at the surface of an O_2-overvoltage anode [16-21] :

$$H_2O \rightarrow {}^\bullet OH_{ads} + H^+ + e^- \quad \text{(acid or neutral media)} \quad (1)$$

$$OH^- \rightarrow {}^\bullet OH_{ads} + e^- \quad (pH \geq 10) \quad (2)$$

The hydroxyl radicals thus formed are one of the most reactive free radicals and one of the strongest oxidants ($E°_{({}^\bullet OH/H_2O)}$ =2.8 V/ENH) next to elemental fluorine. They are stable over a wide pH range, up to pH 10 and react with organic by three principal mechanisms: hydroxyl addition, hydrogen abstraction and electron transfer [22].

Recently, there is a growing interest to the use of BDD as anode material in AO instead of usual anode such as Pt [23, 24, 25], Ti/SnO_2-Sb, Ti/RuO_2 [24], PbO_2 [25], Nb-PbO_2 [26], IrO_2 [25], Ti/RuO_2-IrO_2 [27] and SnO_2 [28]. In fact, this material presents many important characteristics such as an inert surface with low adsorption properties, an extremely wide potential window in aqueous media and a remarkable corrosion stability [29]. Also, it has greater O_2-overvoltage than the Pt anode allowing the production of larger amounts of OH giving a complete mineralization of a variety of organic compounds such as propham [30], clofibric acid [20], chlorophenoxy herbicides [31], 2,4-dichlorophenoxy propionic acid [32], paracetamol [33], cresols [21], gallic acid [34], benzoic acid [35], diuron and 3,4-dichloroaniline [36], mecoprop [37], 2,4-dinitrophenol [38] and orange G [39].

Pesticides encompass an array of compounds widely used in agriculture and other settings, resulting in continuing human exposure. Pesticides are considered as pollutants of natural waters and soil in application sites. They are toxic and resist biodegradation. In addition, it has been shown that pesticides exposure predisposes to cancer and neurodegenerative disease. Among a large variety of compounds rotenone and paraquat are two pesticides used world-wide on a large scale. In fact, rotenone is a botanical insecticide obtained from the roots of many tropical plants of the genera *Derris*, *Tephrosia* and *Lonchocharpus*. It is employed for the protection of many horticultural and fruit crops. Nowadays, it is considered as highly toxic (class I) by the European organic agriculture (EPA) and it is used with a strong restriction regarding its environmental hazards. Paraquat is a nonselective bipyridyl contact herbicide used primarily for wood and grass. It is extremely toxic and can cause human lethal responses in both animals and humans after acute exposure [40].

Several epidemiological studies have reported a positive association between the exposure to these two hazardous compounds and the development of Parkinson disease [41-47].

In order to avoid their possible adverse health effects on humans and animals, it is necessary to remove them completely by the use of powerful oxidative methods. Consequently, we have recently reported the efficient mineralization of these two compounds by anodic oxidation, electro-Fenton and photoelectron-Fenton methods using a Pt anode [48, 49].

In this paper, we studied their degradation by anodic oxidation using a BDD anode and a carbon felt cathode for the first time in literature. Furthermore, the simultaneous effect of dissolved oxygen and hydroxyl radicals on the degradation process is investigated. The decay of pesticides and the evolution of their by-products such as aromatics, carboxylic acids and inorganic ions were followed by chromatographic techniques.

EXPERIMENTAL

1. Chemicals

Rotenone, paraquat, benzophenone were reagent grade, with purity > 98%, supplied by Sigma-Aldrich. Formic, acetic, oxalic and succinic acids were purchased from Fluka. Anhydrous sodium sulfate, potassium nitrate and potassium chloride were analytical grade purchased from Merck and Across Organics.

All solutions were prepared with high-purity water obtained from a Millipore milli-Q system (resistivity > 18 MΩ cm at 25°C). Analytical grade sulfuric acid from Prolabo was used to adjust its initial pH to 3.0. Organic solvents and other chemicals used were either HPLC or analytical grade from Prolabo, Merck and Sigma-Aldrich. Impurity-free oxygen and nitrogen were used to maintain the solution oxygen-saturated or deoxygenated.

2. Electrochemical Cell

All electrolyses were conducted in an undivided and thermostated cylindrical glass cell containing a 100 mL solution stirred with magnetic bar and equipped with two electrodes. The cathode was a (3cm×5cm) carbon felt obtained from Carbone Lorraine and the anode was a BDD thin film deposited on both sides of a niobium substrate (7cm×12cm) obtained from Magneto Chem. The anode was centered in the electrolytic cell, surrounded by the cathode.

The degradation experiments were performed by using aqueous solutions of paraquat (20 mg L^{-1}) and aqueous-acetonitrile mixture (70:30) of rotenone (20 mg L^{-1}). The pH value of 3.0 was chosen since it is close to the optimum pH 2.8 of Fenton reaction. The effect of dissolved oxygen on the degradation of the two pesticides was studied by applying a constant current (I=100 mA) under continuous or without O_2 bubbling. The effect of the supporting electrolyte was also explored by using the following salts: Na_2SO_4 (0.05 mM) and NaCl (0.05 mM). In addition, various electrolyses were performed at constant current (I) of 50, 100, 200 and 300 mA at 25° C to investigate its effect on AO treatment.

All experiments were carried out under continuous agitation of the solution with a magnetic bar to ensure its homogenization and samples were withdrawn from the reaction medium at regular time intervals.

3. Instruments and Analytical procedures

All anodic experiments were carried out with an EG&G Princeton Research 173 A potentiostat-galvanostat. Solutions pH were measured with a Eutech Instruments Cyber Scan pH 1500 pH-meter. The decay of the rotenone concentration was followed by HPLC using a Merck Hitachi Lachrom system equipped with a L-2400 UV detector selected at λ=296 nm and a reverse phase Purospher RP -18, 5 µm, 4.6 × 250 mm column thermostated at 40°C. These analyses were carried out by injecting 20 µL samples into the chromatograph under circulating of a 60:40 (V/V) acetonitrile/water as mobile phase at 1 mL/min. Under these conditions, the rotenone peak was quantified at retention time of 9.0 min and λ=296 nm whereas the resulting by-products peaks were analyzed at t_R= 4.7 min, t_R= 4.9 min and t_R= 6.75 min.

Measurements of paraquat decay and the evolution of its aromatic intermediates were conducted using the same HPLC chromatograph, a 25:75, (V/V) acetonitrile/ decansulfonic acid (75%)/ NaCl (0.1 M) (pH=2.5) mixture at 1 mL/min was employed as mobile phase. The most three dominant intermediates were eluted at t_R= 4.4 min, t_R= 4.9 min and t_R= 5.2 min before the paraquat peak (t_R= 7.6 min) at λ=296 nm.

The generated carboxylic acids were identified and quantified by a supelcogel H column (9µm, 25 cm×4.6mm (i.d)) at 40°C. H_2SO_4 (4mM) was used as mobile phase with a flow rate of 0.2 mL/min. Detection was performed at λ=210 nm.

The concentration of chloride and nitrate ions released during paraquat electrolyses were determined by ion chromatography (Dionex ICS-1000) fitted with an anionic exchanger column (AS4A-SC), 4 mm×250 mm and coupled with a DS 56 conductivity detector at

35°C and ë=210 nm. A solution of potassium carbonate (1.8 mM) and sodium bicarbonate (1.7 mM) were employed as mobile phase.

The mineralization of paraquat treated solutions was monitored by the abatement of their organic carbon (TOC), determined on a Shimadzu VCSN TOC analyzer. Reproductible TOC values were always obtained using the standard NPOC (Non Purgeable Organic Carbon) method.

The COD removal of the treated rotenone solutions were determined using an adapted procedure of the standard method [50].

RESULTS AND DISCUSSION

In order to emphasize the role of molecular oxygen on the mineralization of rotenone and paraquat, experiments were performed in absence and in presence of continuous oxygen bubbling in the solutions. Comparative results corresponding to the mineralization of the two pesticides are shown in Fig. 1a and 1b.

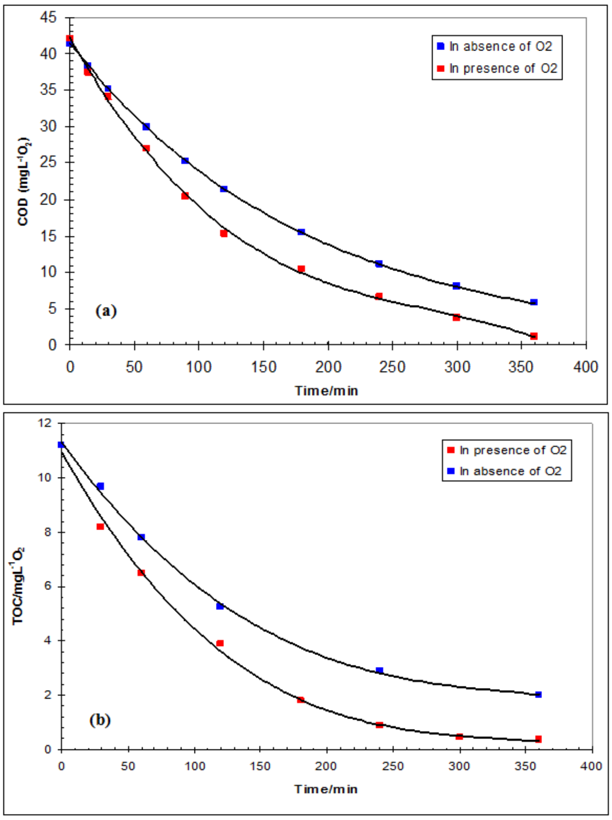

Figure 1. COD (a) and TOC (b) decays upon treatment time by anodic oxidation on BDD in absence and in presence of dissolved O_2. Experimental conditions: (a) $[Na_2SO_4] = 0.05M$ in acetonitrile–water (30/70, v/v), pH= 3.0, $[Rotenone]_0=20mgL^{-1}$ and I=100mA. (b) $[Na_2SO_4] = 0.05M$, pH= 3.0, $[Paraquat]_0=20mgL^{-1}$ and I=100mA.

These results show an increase of the mineralization efficiency in presence of dissolved oxygen (the percentages of DCO and TOC removal were 11% and 18% higher than those obtained in absence of dissolved oxygen).

These findings provide direct evidence that molecular oxygen dissolved in the solutions contributes to the mineralization of the two pesticides on the BDD anodes. In fact, Kaplaka et al. [51] have previously demonstrated that the reaction with oxygen initiated electrochemically on BDD electrodes in the presence of organic compound occurs in different steps: (i) water discharge to hydroxyl radical $^{\cdot}OH$; (ii) dehydrogenation of organic compound RH via $^{\cdot}OH$ and formation of free organic radical $R^{\cdot}$; (iii) addition of molecular oxygen to $R^{\cdot}$ resulting in formation of an organic peroxy radical $RO_2^{\cdot}$ which are very reactive and capable to initiate subsequent chain reactions leading to complete mineralization of RH.

Taking into account the above results, the influence of other experimental parameters on the degradation process were examined in O_2 saturated solutions of rotenone paraquat.

1. Effect of supporting electrolyte nature

A series of experiments were performed by electrolyzing solutions of paraquat and rotenone of pH 3.0 at 100 mA containing either 0.05 mM Na_2SO_4 or 0.05 mM NaCl.

Fig. 2 a reveals that the degradation rate of rotenone was enormously increased when NaCl is used as the supporting electrolyte instead of Na_2SO_4. In fact, about 98% of initial insecticide concentration is destroyed during the first 10 minutes of the AO-BDD treatment and only 40 min was needed for total disappearance of this pollutant. In contrast, when Na_2SO_4 is used as supporting electrolyte, a small decrease (~ 23%) was observed in the degradation rate of rotenone after 10 min of electrolysis time and its complete destruction exceeds 210 min. The obtained results in the case of NaCl can be explained by the parallel participation of powerful oxidants of active chlorine such as Cl_2 (reaction 4 and 5) and HClO (reaction 5) formed by the oxidation of the chloride ions at the BDD anode. These reactive species react with rotenone and enhanced its degradation kinetics:

$$Cl^- \longrightarrow Cl^-_{ads} + e^- \qquad (3)$$
$$Cl^-_{ads} + Cl^- \longrightarrow Cl_2 \qquad (4)$$
$$Cl_2 + H_2O \longrightarrow HClO + H^+ + Cl^- \qquad (5)$$

However, this phenomenon decreases the production of hydroxyl radicals which are the most powerful oxidants and then reduces the mineralization efficiency. In contrast, the degradation rate of paraquat was performed in presence of Na_2SO_4 (Fig.2 b). The obtained results indicate clearly that a total disappearance of paraquat occurs after 120 min of electrolysis in the presence of Na_2SO_4 whereas approximately 35% of its initial concentration remained in the solution at the same time in the presence of NaCl. The observed behavior may be explained may be due to the lowest oxidative ability of Cl_2 and $HClO^-$ coming from the oxidation of Cl^- as compared to •OH radicals and persulfates ions obtained from the oxidation of sulfates ($E^\circ(S_2O_8^{2-}/SO_4^{2-})=2V$). Moreover, an eventual role of acetonitrile can be considered.

2. Effect of applied current

The influence of the applied current on the degradation rate of rotenone and paraquat were further studied by electrolyzing a series of 20 mg L^{-1} pesticides solutions of pH 3.0 at 50, 100, 200 and 300 mA.

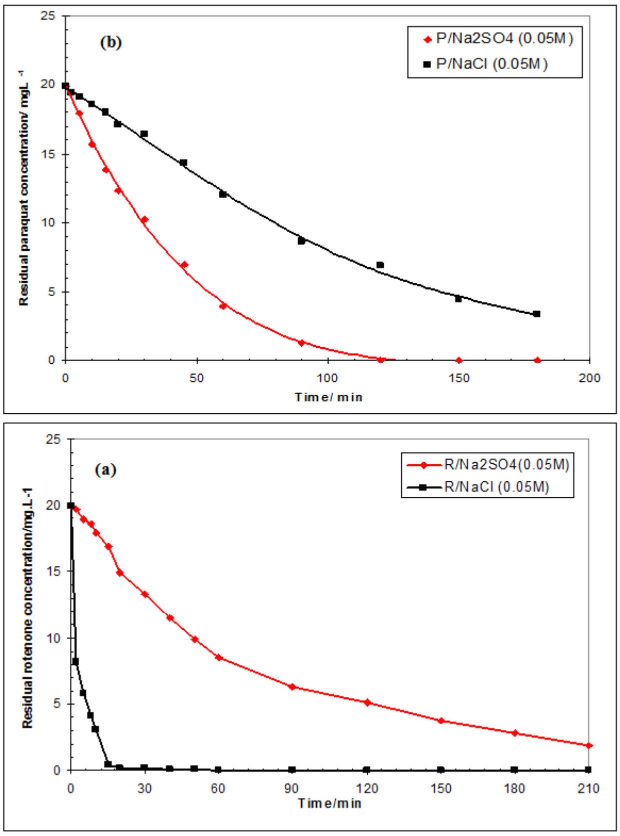

Figure 2. Effect of the nature of supporting electrolyte on the removal of rotenone (a) and paraquat (b), during anodic oxidation treatment. Experimental conditions: $[Na_2SO_4] = [NaCl] = 0.05M$, pH=3.0, V_0=250 mL, $[Rotenone]_0 = [Paraquat]_0 =$ 20 mg L^{-1} and I=100 mA.

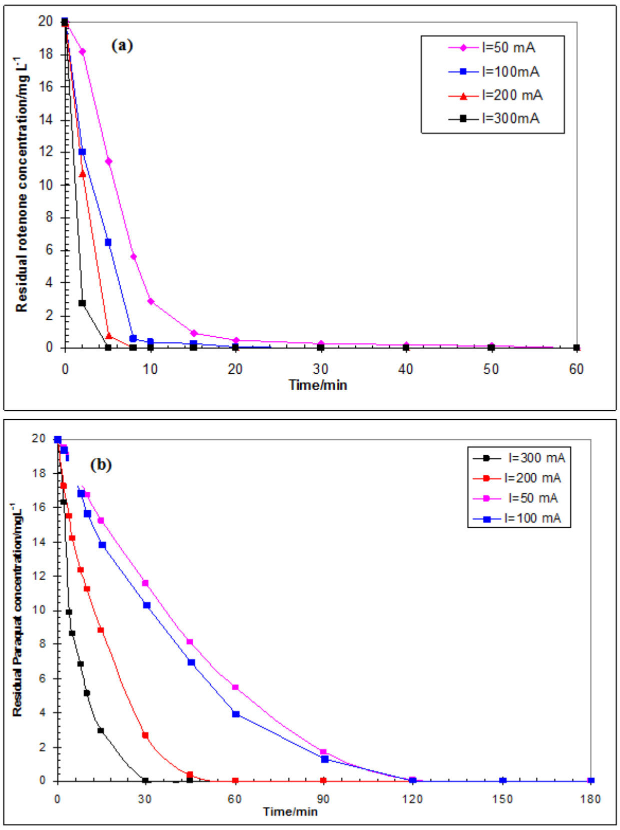

Figure 3. Effect of current intensity on the removal of rotenone (a) and paraquat (b) during anodic oxidation treatment. Experimental conditions:
a) $[Na_2SO_4] = 0.05$ M in acetonitrile-water (30/70, v/v), pH = 3.0, V_0 = 250 mL, $[Rotenone]_0$ = 20 mg L^{-1}.
(b) $[NaCl] = 0.05$ M, pH = 3.0, V_0 = 250 mL, $[Paraquat]_0$ = 20 mg L^{-1}.

As can be seen in Fig. 3 a and 3 b, a significant increase in the degradation rate of rotenone and paraquat were obtained by increasing the applied current values from 50 to 300 mA. This trend can be ascribed by the rapid reaction of pesticides with the concomitant higher concentration of hydroxyl radicals produced and adsorbed on the BDD anode (see reaction 1). On the other hand, mineralization yields (Fig. 4 a and 4 b) are slightly affected by the increase of applied current. Small enhancement of COD abatement (from 97% for R and 94% for P to 98% for R and 97% for P after 6h) is effected by increasing current intensities from 100 mA to 300 mA. This behavior can be attributed to the fact that H_2O_2 produced at the cathode is a scavenger of •OH.

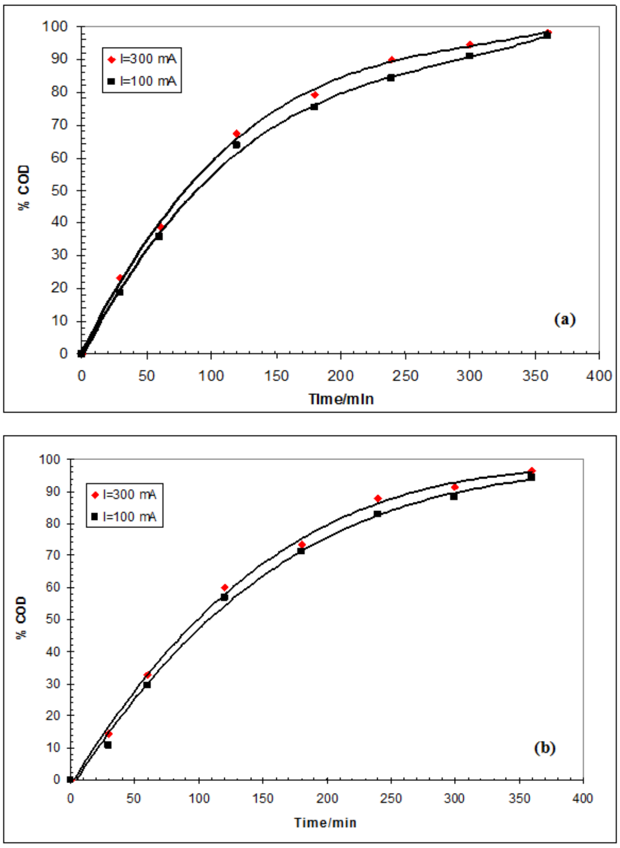

Figure 4. Comparison of COD abatement at I=100 mA and I=300 mA during anodic oxidation treatment of rotenone (a) and paraquat (b). Experimental conditions: (a) $[Na_2SO_4] = 0.05$ M in acetonitrile-water (30/70, v/v), pH = 3.0, $V_0 = 250$ mL, $[\text{Rotenone}]_0 = 20$ mg L^{-1}. (b) [NaCl] = 0.05 M, pH = 3.0, $V_0 = 250$ mL, $[\text{Paraquat}]_0 = 20$ mg L^{-1}.

3. Decay kinetics of paraquat and rotenone

The absolute second-order rate constant for the reaction between each pesticide and •OH in solution was determined using the competition kinetic method [51]. This study was carried out by electrolyzing an aqueous-acetonitrile solution (30:70) of rotenone (20 mg L^{-1}), paraquat (20 mg L^{-1}) with 0.05 M Na_2SO_4 of pH 3.0 at 100 mA. Benzophenone (25 mg L^{-1}) was taken as standard competition substrate for which the absolute rate constant is: K_{BPh}= 8.8 10^9 $M^{-1}s^{-1}$ [52]. The time course of the concentration of these compounds during electrolysis is given in Fig.5. As shown in the inset panel of Fig. 5, pseudo first order kinetic law was found for the third compounds. Apparent rate constant values of rotenone, paraquat and benzophenone were determined from the slope of the corresponding straight lines as 0.1944 min^{-1}, 0.0271 min^{-1} and 0.0481 min^{-1}. This leading to the calculated values of $K_{abs(rotenone)}$=3.55 10^{10} $M^{-1}s^{-1}$ and $K_{abs(paraquat)}$ =1.23 10^9 $M^{-1}s^{-1}$. The obtained results confirm that the reactivity of rotenone towards •OH is much higher than the one of paraquat towards •OH and explain the fast disappearance of rotenone.

4. Evolution of aromatic intermediates

The aromatic products formed during the oxidation of two pesticides were detected by

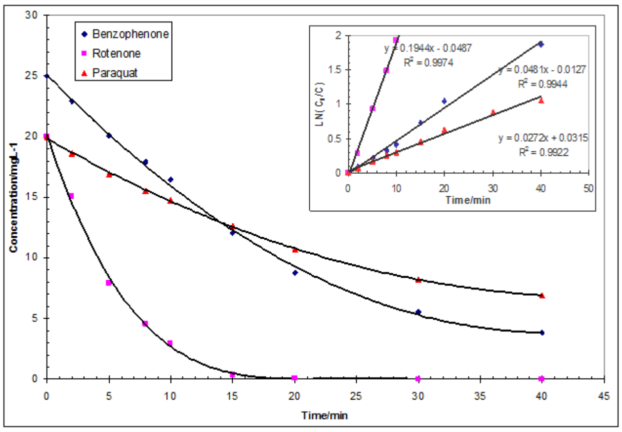

Figure 5. Competitive degradation kinetics of rotenone, paraquat and benzophenone by anodic oxidation treatment.
Experimental conditions: [NaCl] = 0.05 M, pH = 3.0, V_0=250 mL, $[\text{Paraquat}]_0 = [\text{rotenone}]_0$ =20 mg L^{-1}, $[\text{Bph}]_0$ = 25 mg L^{-1}, I = 50 mA and T=25°C.

HPLC. The obtained chromatograms recorded for the rotenone treated solution displayed three well-defined peaks. These aromatic were observed previously during an EF treatment of rotenone and two of them were identified as hydroquinone and 12aβ-hydroxyrotenone with retention times of 4.9 min and 6.75 min, respectively [48]. Fig. 6 a shows that the three oxidation products are accumulated in 10 min and completely removed after 40-50 min of electrolysis.

Several intermediates were also detected during the anodic oxidation of a paraquat solution. Fig. 6 b exhibits the evolution of three different paraquat metabolites in function of treatment time. P_1, P_2 and P_3 appear in the first 6 min of electrolysis and their concentrations reache a maximum value of approximately 10, 10 and 2 min respectively. Complete disappearance of these aromatic was observed in less than 50 min.

5. Evolution of carboxylic acids and inorganic ions

The short carboxylic acids generated from rotenone and paraquat degradation came from the destruction of aromatics intermediates. Ions -exclusion HPLC chromatograms of rotenone and paraquat treated solutions displayed four main peaks related to formic, acetic, oxalic and succinic acids. These acids were observed previously during Electro-Fenton treatments of the two pesticides [48, 49]. The time course of the concentration of the identified acids are presented in fig. 7a and 7b.

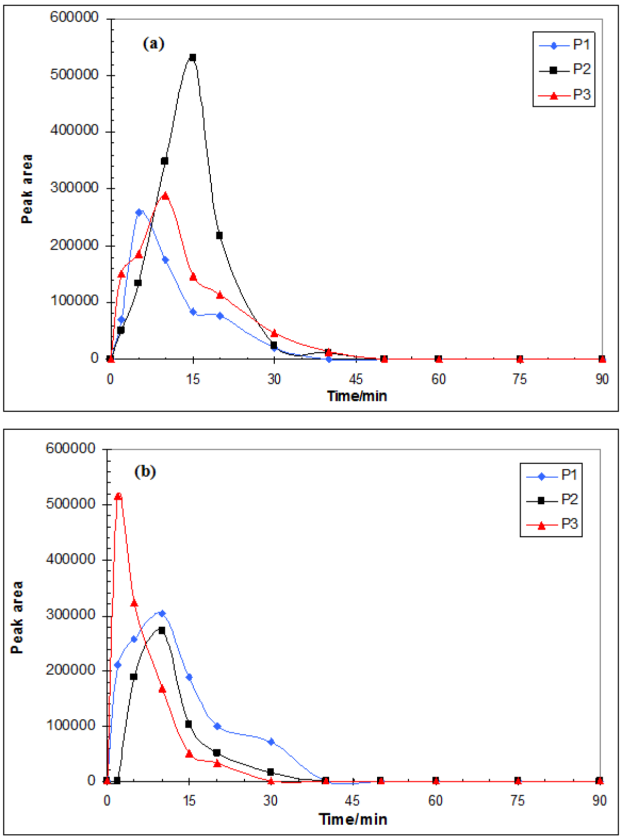

Figure 6. Time evolution of rotenone (a) and paraquat (b) aromatic degradation intermediates during AO treatment. Experimental conditions:
(a) $[Na_2SO_4]$ = 0.05 M in acetonitrile-water (70/30, v/v), pH = 3.0, V_0 = 250 mL, $[rotenone]_0$ = 20 mg L^{-1}, I = 100 mA
(b) [NaCl] = 0.05 M, pH = 3.0, V_0 = 250 mL, $[Paraquat]_0$ = 20 mg L^{-1}, I = 100 mA.

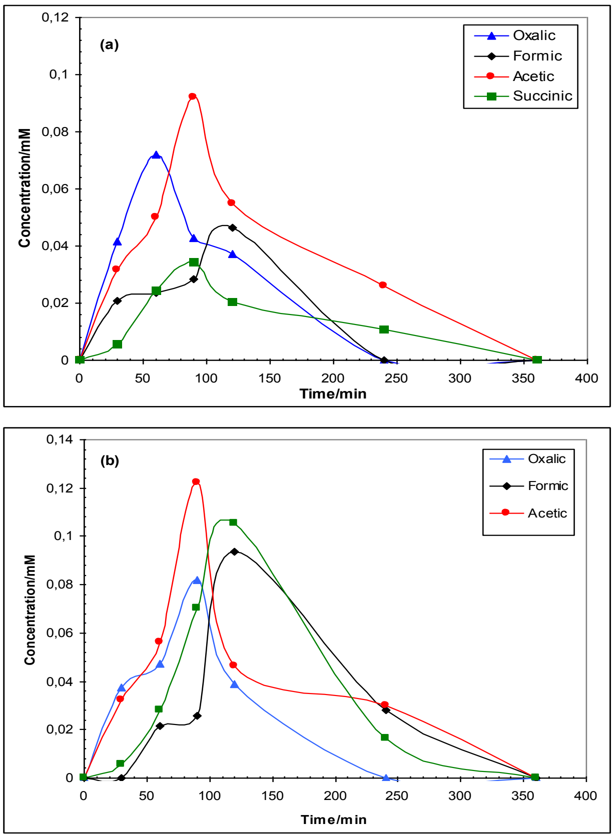

Figure 7. Time evolution of aliphatic carboxylic acids generated during anodic oxidation of rotenone (a) and paraquat (b). Experimental conditions: (a) $[Na_2SO_4]$ = 0.05 M in acetonitrile-water (70/30, v/v), pH = 3.0, V_0 = 250 mL, $[rotenone]_0$ = 20 mg L^{-1}, I = 100 mA
(b) [NaCl] = 0.05 M, pH = 3.0, V_0 = 250 mL, $[Paraquat]_0$ = 20 mg L^{-1}, I = 100 mA.

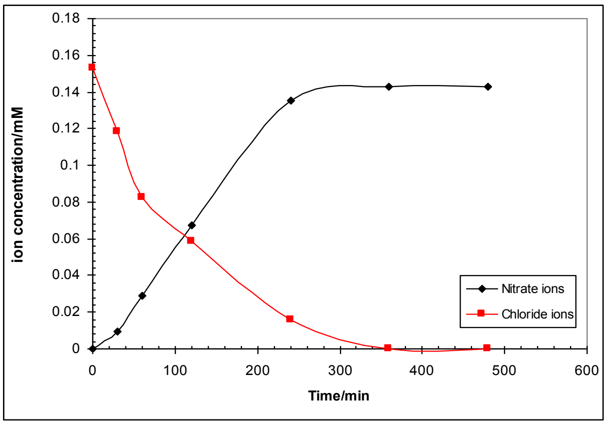

Figure 8. Time evolution of Nitrate and ammonium ions generated during the anodic oxidation treatment of paraquat. Experimental conditions: pH = 3.0, $V_0 = 250$ mL, $[Paraquat]_0 = 20$ mg L^{-1}, I = 100 mA.

As it can be seen, they are formed at the beginning of the treatment and their concentrations reach rapidly a maximum value in the first two hours of electrolysis. An overall disappearance of the detected acids take place after only 6h of treatment. These results prove that the oxidation of the carboxylic acids in the BDD//CF system were faster compared to the Pt//CF system.

The quantification and the evolution of inorganic ions resulting from the mineralization of paraquat were followed by ion chromatography during the anodic oxidation process. Fig. 8 shows that nitrate ions accumulated rapidly in the first 2 hours of the electrolysis, after that time, the formation rate was significantly decreased and reached a steady-state value. The total amount of nitrate ions measured at the end of treatment is equal to 0.142 mM which represents 92% of the theoretical concentration of the initial nitrogen. Moreover, the chloride ion concentration was decreased gradually and disappears at 8h indicating a quasi complete mineralization of paraquat at the end of electrolyses.

CONCLUSION

Anodic oxidation with BDD is a viable technique for the overall decontamination of wastewaters containing rotenone and paraquat. The effect of operational system parameters were investigated. It has been found that the mineralization of two organic compounds on BDD electrodes were significantly enhanced in presence of oxygen-saturated solutions. This occurs via not only hydroxyl radicals adsorbed on BDD electrode but also by peroxy radicals $(RO_2^{\cdot})$ resulting by the addition of molecular oxygen to an organic free radical $(R^{\cdot})$.

The degradation rate of rotenone was fastest in the presence of Na_2SO_4 0.05 mM whereas the use of NaCl 0.05 mM has a prominent effect on the degradation kinetics of paraquat.

The degradation rate of the two pesticides are also enhanced when applied current is increased. This is due to the greater production of •OH on the anode surface from water oxidation or hydroxide ion in acid or alkaline medium.

The decay of the two pesticides follows a pseudo first-order kinetics. HPLC analysis of electrolyzed solutions allows the detection of three aromatic intermediates for each pesticide. Only two of them: hydroquinone and 12aβ-hydroxyrotenone are identified in a previous work as rotenone oxidation by-products. Generated carboxylic acids such as formic, acetic, oxalic and succinic are identified and quantified by ion-exclusion chromatography. All these products are completely destroyed at the end of treatment. The maximum nitrate ions concentration produced corresponds to 92% of the initial nitrogen in solution and all chloride ions are completely oxidize to Cl_2 on the BDD anode. In conclusion, the obtained results show that the AO with BDD is a very effective method for the complete mineralization of paraquat and rotenone obtained thanks to molecular oxygen in aerated solutions.

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