第 19 卷 第 4 期 电化学 Vol. 19 No. 4
2013 年 8 月 JOURNAL OF ELECTROCHEMISTRY Aug. 2013

Artical ID:1006-3471(2013)04-0300-13

Performance of the Electro-Oxidation and Electro-Fenton Processes with a BDD Anode for the Treatment of Low Contents of Pharmaceuticals in a Real Water Matrix

Ignasi Sirés, José Antonio Garrido, Enric Brillas*

(*Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès* 1-11, 08028 *Barcelona, Spain*)

Abstract: Here, we report the performance of electro-oxidation and electro-Fenton with a boron-doped diamond (BDD) anode for the treatment of single and multicomponent solutions containing small amounts of pharmaceutical residues (i.e., 1 mg·L^{-1} paracetamol and/or 1 mg·L^{-1} salicylic acid) spiked into a real water matrix at pH 3.0. Electro-oxidation was performed in a BDD/Pt cell, whereas electro-Fenton was carried out in a BDD/air-diffusion cell to electrogenerate H_2O_2 at the cathode, always operating at constant current density. It was found that the decay of both pharmaceuticals by electro-oxidation was more rapid in the real water matrix than in ultrapure water with 0.05 mol·L^{-1} Na_2SO_4 because of their additional reaction with active chlorine species produced at the bulk from the oxidation of Cl^- ion. Such chlorinated oxidants exhibited even higher reactivity than hydroxyl radicals formed and confined at the anode. The increase in current density largely enhanced the removal of both pollutants. Similar results were found using the real water matrix at natural alkaline pH. When the mixture of both pharmaceuticals was treated by electro-oxidation, their abatement became slower owing to the competitive attack of generated oxidants over them. Only a slight acceleration of pharmaceutical decay was obtained for the real water matrix using electro-Fenton, since the accumulation of additional homogeneous hydroxyl radical formed from Fenton's reaction between generated H_2O_2 and added Fe^{2+} was inhibited by its reaction with Cl^- to form much less reactive chlorinated radicals. For the real water matrix with added pharmaceuticals, a high degree of mineralization of the natural organic matter content (NOM) was reached at high current densities by electro-oxidation, which was even improved upon addition of 0.05 mol·L^{-1} Na_2SO_4. Traces of oxidation by-products like *p*-benzoquinone, as well as NO_3^- and NH_4^+ ions, were detected during the electro-oxidation of paracetamol solutions, but the N-compounds contained in the real water matrix were not removed under the investigated conditions.

Key words: boron-doped diamond anode; electro-oxidation; electro-Fenton; paracetamol; real water matrix; salicylic acid

CLC Number: O646 **Document Code:** A

Over the last fifteen years, pharmaceutical drugs have received increasing attention as potential bioactive chemicals in the environment[1]. They are considered as emerging pollutants in waterbodies because they remain unregulated or their directives and legal frameworks are not yet set-up[2]. Pharmaceuticals and their metabolites are continuously introduced in the aquatic environment, where they are detected at trace concentrations (i.e., as micropollutants found in the ng·L^{-1} or μg·L^{-1} range). This pollution arises from emission from production sites, direct disposal of overplus drugs in households and hospitals, excretion

Received: 2012-12-25, Revised: 2013-02-28 *Author for correspondence: Tel.: +34 93 4021223, Fax: +34 93 4021231, E-mail: brillas@ub.edu

This work was supported by project CTQ2010-16164/BQU co-financed with Ministerio de Ciencia e Innovación (MICINN, Spain) and FEDER funds.

from urine or faeces after drug administration to humans and animals, and water treatments in fish farms[3]. Pharmaceuticals persist in the environment mainly because of their incomplete elimination in sewage treatment plants (STPs), with 60% to 90% of the parent molecules still present after the action of biodegradation, deconjugation, partitioning, and photodegradation steps[4]. This affects the water quality and drinking water supply, and may constitute a potential risk for the ecosystems, the human and animal welfare in the long term[5]. Although the effects of pharmaceuticals on living beings are not well documented[1], several studies have shown that they may cause slow but irreversible changes to the genome sequence of microorganisms, which increases their resistance to them[2, 5]. Also, some drugs classified as endocrine disrupting compounds (EDCs) cause harmful effects on the human endocrine system[2, 5-6]. To avoid their potential toxicity and other possible dangerous health effects, the removal of pharmaceuticals and their metabolites from waters must be ensured by developing more powerful oxidation methods.

Recently, a large variety of electrochemical advanced oxidation processes (EAOPs) have been developed to mineralize persistent and toxic organics found in waters[3, 7-8]. EAOPs are able to electrogenerate the hydroxyl radical (•OH), the second strongest oxidant known after fluorine. It has such a high standard reduction potential (E^o(•OH/H_2O) = 2.80 V/SHE at 25 ºC) that can non-selectively react with most organics giving dehydrogenated or hydroxylated derivatives, which can eventually be completely mineralized to CO_2, water and inorganic ions[7-9]. The simplest and most common EAOP for water remediation is electro-oxidation, in which organics contained in a contaminated solution are oxidized by direct charge transfer at the anode (M), or rather destroyed with physisorbed hydroxyl radical (M(•OH)) formed as intermediate of O_2 evolution from water oxidation at high current densities[7, 10]:

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e \quad (1)$$

The best anode for electro-oxidation is the boron-doped diamond (BDD) thin-film electrode, which possesses technologically important properties like an inert surface with low adsorption properties, remarkable corrosion stability even in strongly acidic media, and extremely high O_2-evolution overvoltage. These characteristics enhance the removal of organics with reactive BDD(•OH)[7], and confer to the BDD anode a high ability to mineralize aromatic pollutants[3, 7, 9-13] and their by-products, i.e., aliphatic carboxylic acids[14-15], showing much higher oxidation power than traditional anodes like Pt[12] and PbO_2[16].

EAOPs based on H_2O_2 generation have also received great attention for water treatment[8]. The most popular of these methods is electro-Fenton, which involves the continuous supply of H_2O_2 to an acidic contaminated solution from the two-electron reduction of O_2 gas at a carbonaceous cathode, usually carbon felt[17-22] or carbon-polytetrafluoroethylene (PTFE) gas (O_2 or air) diffusion electrodes[17, 18, 23-25]:

$$O_{2(g)} + 2H^+ + 2\,e \rightarrow H_2O_2 \quad (2)$$

In electro-Fenton, a catalytic amount of Fe^{2+} is added to the solution to react with H_2O_2 giving homogeneous •OH and Fe^{3+} from Fenton's reaction (3). This reaction is catalytic and is mainly propagated by the cathodic reduction of Fe^{3+} to Fe^{2+} from Reaction (4)[3, 8].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (3)$$

$$Fe^{3+} + e \rightarrow Fe^{2+} \quad (4)$$

Thus, the electro-Fenton process in an undivided cell with a BDD anode involves the attack of organics by both, heterogeneous BDD(•OH) formed from Reaction (1) and homogeneous •OH produced in the bulk from Fenton's reaction (3).

In previous works, we have applied the electro-oxidation and electro-Fenton processes to effectively mineralize high contents of several pharmaceuticals or metabolites, including triclosan[17], triclocarban[17], chlorophene[18], clofibric acid[23], ibuprofen[24], paracetamol (N-(4-hydroxyphenyl)acetamide)[11, 25-26], and salicylic acid (2-hydroxybenzoic acid)[27] in synthetic water matrices. However, much less is known about the viability of these processes for the treatment of low concentrations of pharmaceuticals in surface and ground waters. These aqueous effluents contain natural organic matter (NOM), which is all the

organic matter in a reservoir or natural ecosystem other than living organisms and man-made compounds, so it includes a wide variety of dissolved complex molecules like humic, fulvic, and tannic acids, as well as polysaccharides, among other substances[28]. This dissolved fraction of NOM is hardly oxidized, not being fully removed upon application of conventional water processes in STPs. Lately, more efficient AOPs have emerged for the removal of NOM, aiming to avoid many serious problems related to its presence when water treatments are applied[29-30]. To clarify the influence of NOM on the oxidation ability of the above EAOPs, we have undertaken a study on the removal of paracetamol and salicylic acid spiked into a real water matrix. Paracetamol, a common analgesic and anti-inflammatory for humans and animals, has been found with concentrations < 10 $\mu g \cdot L^{-1}$ in European[31] and Australian[32] STP effluents, as well as in USA natural waters[33]. Salicylic acid, easily produced from hydrolytic deacetylation of the drug acetylsalicylic acid (aspirin), is accumulated in STP effluents and natural waters[31-32, 34]. Other authors have also shown that paracetamol and salicylic acid can be degraded by both, electro-oxidation with different anodes[32, 35-36] and electro-Fenton[37] in synthetic aqueous matrices.

This paper reports the performance of two EAOPs, electro-oxidation and electro-Fenton with a BDD anode, for the treatment of 1 $mg \cdot L^{-1}$ of paracetamol and salicylic acid, alone or mixed, upon addition to a real water matrix. Comparative experiments with ultrapure water were made to study the influence of NOM on the processes. Electro-oxidation was tested with BDD/Pt and BDD/air-diffusion cells to investigate the influence of electrogenerated H_2O_2 on the degradation ability. The effects of current density (j) and Na_2SO_4 content on electro-oxidation performance were also examined.

1 Materials and Methods

1.1 Chemicals

Paracetamol was of reagent grade from Sigma-Aldrich. Salicylic acid, as well as ferrous sulfate heptahydrate used as a catalyst, was of analytical grade from Fluka. Anhydrous sodium sulfate, used as background electrolyte, and sulfuric acid, used to adjust the initial pH of solutions, were of analytical grade from Merck. Synthetic solutions were prepared with ultrapure water obtained from a Millipore Milli-Q system with resistivity > 18 $M\Omega \cdot cm$ at 25 ºC. Organic solvents and other chemicals used were either of HPLC or analytical grade supplied by Aldrich, Merck, and Panreac.

1.2 Electrolytic Systems

All the electrolytic experiments were conducted in an open, undivided cylindrical cell of 150 mL capacity, equipped with a double jacket where external thermostated water was recirculated to maintain the solution temperature at 25 ºC. Solutions of 100 mL with 1 $mg \cdot L^{-1}$ paracetamol and/or salicylic acid were electrolyzed under vigorous stirring with a magnetic bar at 400 rpm to ensure mixing and the transport of reactants towards/from the electrodes. The anode was always a BDD electrode purchased from Adamant Technologies, synthesized by the hot filament chemical vapor deposition technique on single-crystal p-type Si(100) wafers (0.1 $\Omega \cdot cm$, Siltronix). The cathode was either a Pt sheet purchased from SEMPSA, used in the majority of electro-oxidation experiments, or a carbon-PTFE air-diffusion electrode supplied by E-TEK for electro-Fenton as well as for some electro-oxidation experiments. This air-diffusion cathode was mounted as described elsewhere[38] and was fed with air pumped at 300 $mL \cdot min^{-1}$ to generate H_2O_2 from Reaction (2). The geometric area of all the electrodes was 3 cm^2, and the separation between the anode and cathode in both BDD/Pt and BDD/air-diffusion cells was close to 1 cm. The assays were performed at constant j of 10 or 50 $mA \cdot cm^{-2}$, using an Amel 2053 potentiostat-galvanostat as a current source. The potential difference of the cell was directly measured on a Demestres 653B digital multimeter. In order to remove the impurities of the BDD surface and activate the air-diffusion cathode, they were previously polarized in 0.05 $mol \cdot L^{-1}$ Na_2SO_4 solution at 100 $mA \cdot cm^{-2}$ for 60 min. Electro-Fenton treatments were made for solutions of pH 3.0 after

addition of 0.15 mmol·L^{-1} Fe^{2+}. Such values of solution pH and Fe^{2+} concentration were chosen because they were found to be the optimal ones for similar degradation studies of high concentrations of paracetamol[26] and salicylic acid[27] in synthetic solutions.

1.3 Instruments and Analytical Procedures

The solution pH was measured with a Crison GLP 22 pH-meter. Samples were withdrawn at regular time periods from treated solutions and microfiltered with 0.45 μm PTFE filters (Whatman) before analysis. Total carbon was determined with a Shimadzu VCSN TOC analyzer. This system was also used for assessing the mineralization of solutions from their dissolved organic carbon (DOC) decay measured with the non-purgeable organic carbon (NPOC) method. Reproducible DOC values with ±1% precision were found by injecting 50 μL aliquots into the TOC analyzer. Total nitrogen (TN) was obtained with a Shimadzu TNM-1 unit coupled to this analyzer.

Paracetamol and salicylic acid removals were assessed by reversed-phase HPLC using a Waters 600 LC fitted with a Thermo BDS Hypersil C18 5 μm, 250 mm × 4.6 mm, column at 35 ºC, and coupled to a Waters 996 photodiode array detector selected at the λ_{max} of the UV spectra of each compound. These analyses were made with a 30:70 (*V*/*V*) acetonitrile/water (phosphate buffer of pH 3.25) mixture at 0.6 mL·min^{-1} as mobile phase, showing well-defined peaks for paracetamol at retention time (t_r) = 5.8 min and λ = 246 nm, salicylic acid at t_r = 8.8 min and λ = 234 nm, and *p*-benzoquinone at t_r = 7.9 min and λ = 244 nm.

Metal cations (Mg^{2+}, Ca^{2+}, and iron ions) were quantified by inductively coupled plasma-optical emission spectrometry (ICP-OES) with a Perkin Elmer Optima 3200RL system. Other inorganic ions were detected by ion chromatography using a Shimadzu 10 Avp HPLC coupled to a Shimadzu CDD 10 Avp conductivity detector. Concentrations of Na^+, K^+, and NH_4^+ were obtained by using a Shodex IC YK-421, 125 mm × 4.6 mm, cation column under circulation of a mobile phase of 5.0 mmol·L^{-1} tartaric acid, 2.0 mmol·L^{-1} dipicolinic acid, 24.2 mmol·L^{-1} boric acid, and 15.0 mmol·L^{-1} crown ether at 1.0 mL·min^{-1} and 40 ºC. Contents of Cl^-, ClO_3^-, NO_3^-, and SO_4^{2-} were determined using a Shim-Pack IC-A1S, 100 mm × 4.6 mm, anion column and a 2.4 mmol·L^{-1} tris(hydroxymethyl)aminomethane, and 2.5 mmol·L^{-1} phthalic acid solution of pH 4.0 at 1.5 mL·min^{-1} and 40 ºC as mobile phase.

1.4 Real Water Matrix

The raw water matrix was collected from the primary decantation effluent of a municipal STP in Manresa (Barcelona, Spain) and conserved in a refrigerator at 4 ºC before the degradation assays. The characteristics of this real water are summarized in Tab. 1. As can be seen, the total carbon was very high compared to DOC (which was due to dissolved NOM alone), thus suggesting the presence of large amounts of HCO_3^- and CO_3^{2-} ions in the raw water at such an alkaline pH. Its conductance was very low compared to that of a 0.05 mol·L^{-1} Na_2SO_4 solution (10.5 mS), because of the small content of inorganic salts. No ClO_3^-, NO_3^-, NH_4^+, and iron ions were detected, whereas relatively high concentrations of Cl^- were found, which can presumably affect the oxidation ability of the EAOPs under study[3, 7-8].

Tab. 1 Main physicochemical characteristics of the real water matrix obtained from a municipal STP

Parameter	Value
Total carbon/(mg·L^{-1})	180
DOC/(mg·L^{-1})	8.0
Total nitrogen/(mg·L^{-1})	9.0
Conductance, G (mS)	1.7
pH	7.9
[Na^+]/(mg·L^{-1})	159
[K^+]/(mg·L^{-1})	52
[Ca^{2+}]/(mg·L^{-1})	111
[Mg^{2+}]/(mg·L^{-1})	24
[Iron ions]/(mg·L^{-1})	Not detected
[Cl^-]/(mg·L^{-1})	273
[SO_4^{2-}]/(mg·L^{-1})	189

2 Results and Discussion

2.1 Electro-Oxidation of Solutions Containing Paracetamol Alone

Fig. 1 shows the comparative decay of 1 mg·L^{-1} of paracetamol from both, synthetic solutions with 0.05 mol·L^{-1} Na_2SO_4 and the real water matrix, at different pH values using a BDD/Pt cell at 50 mA·cm^{-2}. As can be seen, this pharmaceutical is completely removed in synthetic solutions by electro-oxidation with a BDD anode, in 45 min at pH 3.0 and more slowly, in 60 min, at natural pH (ca. 6.0). These results indicate the production of slightly higher quantities of oxidant BDD(•OH) from Reaction (1) in the former medium, in agreement with the electrochemical characterization of BDD reported elsewhere[39]. It should be noted that in these trials the solution pH did not vary significantly during the electrolysis times tested. On the other hand, Fig. 1 also shows that paracetamol decay is strongly enhanced using the real water matrix, being removed at a similar rate at both, natural pH (7.9) and pH 3.0, with total disappearance in only 5 min. The large enhancement in the oxidation rate of this pharmaceutical in a real water matrix can be contributed by the generation of active chlorine species from the parallel oxidation of the Cl^- ion (see Tab. 1) at the BDD anode. Therefore, such chlorinated oxidants and BDD(•OH) become competitors. It is well known[7, 40-41] that Cl^- ion is directly oxidized at the BDD anode to yield soluble chlorine by Reaction (5), which diffuses away from the anode to be rapidly hydrolyzed and disproportionated to hypochlorous acid and chloride ion from Reaction (6). Hypochlorous acid is then in equilibrium with hypochlorite ion from Reaction (7) with $pK_a = 7.55$.

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e \quad (5)$$

$$Cl_{2(aq)} + H_2O \rightarrow HClO + Cl^- + H^+ \quad (6)$$

$$HClO \rightarrow ClO^- + H^+ \quad (7)$$

From the above reactions, it can be concluded that the predominant chlorine species in the bulk are Cl_2 up to pH = 3, HClO in pH = 3 ~ 8, and ClO^- at pH > 8[42]. It is thus expected that the mediated oxidation with active chlorine species becomes faster in acid than in alkaline media because of the higher standard potentials of Cl_2 (E^o = 1.36 V/SHE) and HClO (E^o = 1.49 V/SHE) compared to that of ClO^- (E^o = 0.89 V/SHE). However, results of Fig. 1 evidence a fast, quite similar destruction of paracetamol in both acid and alkaline real water matrices, probably due to the great quantities of active chlorine species produced at the high current density of 50 mA·cm^{-2}.

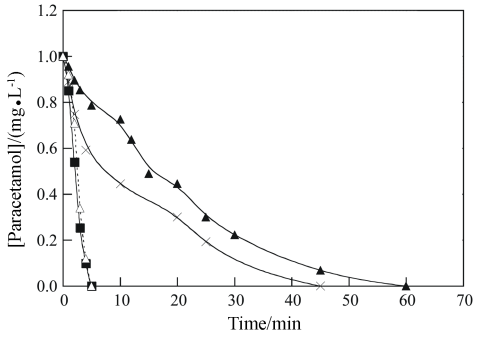

Fig. 1 Paracetamol decay vs. electrolysis time for the electro-oxidation of 100 mL of 1 mg·L^{-1} pharmaceutical solutions in a BDD/Pt cell of 3 cm^2 electrode area at 50 mA·cm^{-2} and 25 ℃ ((▲) Ultrapure water with 0.05 mol·L^{-1} Na_2SO_4 at natural (and uncontrolled) pH, (×) ultrapure water with 0.05 mol·L^{-1} Na_2SO_4 at pH 3.0, (■) real water matrix at natural (and uncontrolled) pH, and (△) real water matrix at pH 3.0)

Note that the oxidation of Cl^- at the BDD anode can also yield other chlorine oxyanions like ClO_2^- from Reaction (8), ClO_3^- from Reaction (9) and/or ClO_4^- from Reaction (10)[7, 43-44]:

$$ClO^- + H_2O \rightarrow ClO_2^- + 2H^+ + 2e \quad (8)$$

$$ClO_2^- + H_2O \rightarrow ClO_3^- + 2H^+ + 2e \quad (9)$$

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e \quad (10)$$

The existence of such reactions during the oxidation of Cl^- was confirmed from the ion chromatography analysis of the real water matrix with 1 mg·L^{-1} paracetamol after 240 min of electro-oxidation in a BDD/Pt cell at 50 mA·cm^{-2}, which revealed about 90% decreases in the initial concentration of Cl^- along with the formation of near 20% ClO_3^-.

The influence of current density on the decay of 1 mg·L^{-1} paracetamol in synthetic and real aqueous matrices of pH 3.0 using the BDD/Pt cell is illustrat-

ed in Fig. 2. A very slow decay in concentration can be observed in ultrapure water at a low j of 10 mA·cm^{-2}, only achieving 64% reduction after 60 min of electro-oxidation. Compared to Fig. 1, the removal rate of the pharmaceutical at 10 mA cm^{-2} is much lower than that at 50 mA·cm^{-2}, where it disappears in 45 min, which can be related to the concomitant lower production of BDD(•OH) from Reaction (1). Nevertheless, it is well known[7,10-11] that the increase in j causes a progressive decrease in the relative amount of BDD(•OH) that is available for the degradation of the organic molecules, which is due to the higher increase in rate of some waste reactions; for example, its anodic oxidation to O_2 from Reaction (11), its dimerization to H_2O_2 from Reaction (12), and its reaction with H_2O_2 generating the weaker oxidant hydroperoxyl radical (BDD(HO_2•)) from Reaction (13). The relative proportion of BDD(•OH) can also diminish by the larger enhancement of Reactions (14) and (15) at high j, giving rise to persulfate ion ($S_2O_8^{2-}$) and ozone, respectively.

$$2BDD(•OH) \rightarrow 2BDD + O_{2(g)} + 2H^+ + 2e \quad (11)$$

$$2BDD(•OH) \rightarrow 2BDD + H_2O_2 \quad (12)$$

$$BDD(•OH) + H_2O_2 \rightarrow BDD(HO_2•) + H_2O \quad (13)$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e \quad (14)$$

$$3H_2O \rightarrow O_{3(g)} + 6H^+ + 6e \quad (15)$$

As shown in Fig. 2, the abatement of paracetamol at 10 mA·cm^{-2} is much faster in the real water matrix, reaching its overall destruction in ca. 60 min, as a result of the combined action of active chlorine species (mainly Cl_2/HClO) and BDD(•OH). This suggests that the former species have a great contribution to the degradation of the organic molecule, due to: (i) their high oxidation power and (ii) the fact that they act in the bulk, instead of being confined in the anode vicinity, in contrast to BDD(•OH). Under these conditions, it should be highlighted that both oxidants can also attack the NOM contained in the real water matrix, as will be discussed below and, consequently, their oxidation ability is lower than using ultrapure water as solvent. Fig. 2 highlights that, at 50 mA·cm^{-2}, the presence of 0.05 mol·L^{-1} Na_2SO_4 in the real water matrix does not modify the rate of paracetamol decay, again yielding total removal in 5 min. This corroborates the predominant role of active chlorine species in the destruction of this pharmaceutical, since the decay kinetics is not affected by the plausible decrease in BDD(•OH) content arising from the acceleration of $S_2O_8^{2-}$ formation from Reaction (14) in the presence of 0.05 mol·L^{-1} Na_2SO_4. It is worth mentioning that the abatement of paracetamol concentration in all the above assays did not follow any kinetic equation related to simple order reactions, thus suggesting the existence of a complex oxidation route for this drug.

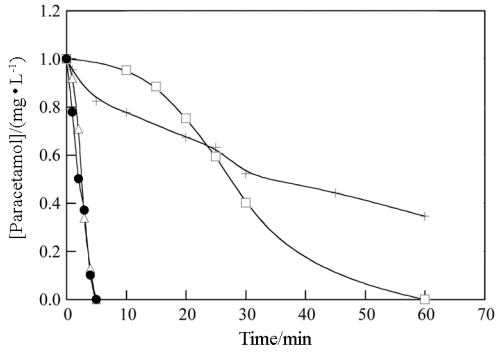

Fig. 2 Time course of paracetamol concentration for the electro-oxidation of 100 mL of 1 mg·L^{-1} of pharmaceutical in solutions of pH 3.0 and 25 ℃ using a BDD/Pt cell ((+) Ultrapure water with 0.05 mol·L^{-1} Na_2SO_4, 10 mA·cm^{-2}, (□) real water matrix, 10 mA·cm^{-2}, (△) real water matrix, 50 mA·cm^{-2}, and (●) real water matrix with 0.05 mol·L^{-1} Na_2SO_4, 50 mA·cm^{-2})

2.2 Electro-Oxidation of Solutions Containing Salicylic Acid Alone

Aiming to confirm the above degradation behavior found for paracetamol, salicylic acid was treated under comparable conditions, so as to ascertain if it can be generalized for the electro-oxidation of low amounts of aromatic drugs with a BDD anode. As can be seen in Fig. 3, the decay of 1 mg·L^{-1} salicylic acid in ultrapure water with 0.05 mol·L^{-1} Na_2SO_4 of pH 3.0 using the BDD/Pt cell was very slow, being faster for 50 mA·cm^{-2} than for 10 mA·cm^{-2}. This is expected from the greater production of the main oxi-

dant BDD(•OH) at higher j values, as pointed out above. The fact that the total destruction of this compound takes place in 60 min at 50 mA·cm^{-2} (see Fig. 3), a time longer than 45 min required for 1 mg·L^{-1} paracetamol under the same conditions (see Fig. 1), is indicative of a slightly slower reaction kinetics between BDD(•OH) and salicylic acid. One can then infer that this radical is potent enough to completely remove low concentrations of aromatic pharmaceuticals in short electrolysis times operating at sufficiently high j values.

When electro-oxidation was performed using the real water matrix, the decay in concentration of salicylic acid was strongly accelerated by its parallel oxidation with active chlorine species produced from Cl^- oxidation by Reaction (5) and thereafter. Fig. 3 high lights that by simply working at a low j of 10 mA·cm^{-2}, this compound was so rapidly destroyed that disappeared in only 7 min. Note that this time is much shorter than 60 min needed for the total abatement of paracetamol under the same conditions (see Fig. 2), evidencing the much faster reaction kinetics between generated active chlorine species (mainly Cl_2/HClO) and salicylic acid. Fig. 3 also shows that increasing j from 10 to 50 mA·cm^{-2} in this medium only yielded a slight acceleration of its removal rate, disappearing in 5 min, in either the absence or the presence of 0.05 mol·L^{-1} Na_2SO_4. These findings allow concluding that in this system, salicylic acid is mainly attacked by active chlorine species, with small contribution of BDD(•OH), so that a j value as low as 10 mA·cm^{-2} is enough to rapidly remove this drug from the medium. In all the experiments, its reaction with generated oxidants was quite complex since it did not follow any kinetic equation related to simple order reactions.

The aforementioned results demonstrate that the current density needed to destroy low contents of aromatic pharmaceuticals in a real water matrix by electro-oxidation with a BDD anode exhibits a great dependence on their reactivity with generated oxidants. Thus, the high oxidation ability of active chlorine species, as well as their distribution in the whole solution bulk that differs from confined BDD(•OH), may enhance the removal of these contaminants allowing the use of lower j values than in non-chloride media to attain their overall disappearance in shorter electrolysis times.

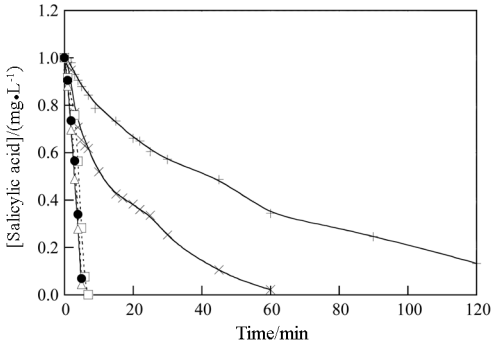

Fig. 3 Removal of salicylic acid with electrolysis time for the electro-oxidation with a BDD/Pt cell of 100 mL of 1 mg·L^{-1} of pharmaceutical in solutions of pH 3.0 and 25 °C ((+) Ultrapure water with 0.05 mol·L^{-1} Na_2SO_4, 10 mA·cm^{-2}, (×) ultrapure water with 0.05 mol·L^{-1} Na_2SO_4, 50 mA·cm^{-2}, (□) real water matrix, 10 mA·cm^{-2}, (△) real water matrix, 50 mA·cm^{-2}, and (•) real water matrix with 0.05 mol·L^{-1} Na_2SO_4, 50 mA·cm^{-2})

2.3 Electro-Oxidation of Multicomponent Solutions with Paracetamol and Salicylic Acid

The electro-oxidation for mixtures of 1 mg·L^{-1} of both, paracetamol and salicylic acid, in synthetic and real matrices was studied to clarify the influence of generated oxidants on each pharmaceutical once it is in competition with the other one. In view of the very fast abatement of salicylic acid in the real water matrix (see Fig. 3), only the changes in paracetamol decay in drug mixture solutions will be described below.

Fig. 4A shows a quicker destruction of paracetamol in a BDD/Pt cell in both synthetic and real solutions when j rises from 10 to 50 mA·cm^{-2} as a result of the larger production of BDD(•OH) and/or active chlorine species due to the acceleration of Reactions (1) and (5), respectively. As expected from the above results, the drug was more rapidly removed in the real

water matrix because of the higher reactivity of active chlorine species formed in this medium. However, comparison in results of Fig. 4A with those of Figs. 1 and 2 for single paracetamol solutions allows inferring a slower decay of this compound in all the mixtures of both pharmaceuticals. For example, after 30 min of electrolysis at 10 mA·cm^{-2} in the synthetic medium, its concentration was reduced by 48% in the single solution (Fig. 2) and by only 37% in the drug mixture (Fig. 4A), whereas at 50 mA·cm^{-2} in the real water matrix, the time for its overall disappearance was prolonged from about 5 min in the single solution (Fig. 1) to near 8 min in the drug mixture (Fig. 4A). This phenomenon can be ascribed to the generation of similar amounts of the corresponding oxidants in each medium under comparable conditions, thereby being competitively consumed by both pharmaceuticals when mixed, so that their individual reaction rates with respect to that of the single drug solutions become slower.

The oxidation ability of other reactive oxygen species (ROS) like H_2O_2 and $HO_2^{\bullet}$ produced during electrolysis from Reactions (12) and (13), respectively, on paracetamol abatement in drug mixture solutions was assessed using a BDD/air-diffusion cell. Under these conditions, H_2O_2 is generated at the cathode from Reaction (2) and accumulated to a large extent in the medium, while it can be oxidized at the anode yielding $HO_2^{\bullet}$[8, 17, 23]

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e \qquad (16)$$

The production of $HO_2^{\bullet}$ from Reaction (16) is much higher than from Reaction (13) due to the much greater generation of H_2O_2 at the cathode from Reaction (2) than at the anode from Reaction (12)[27].

As an example, Fig. 4B depicts the decay in paracetamol concentration in ultrapure water with 0.05 mol·L^{-1} Na_2SO_4 and in real water matrix using a BDD/air-diffusion cell at 10 mA·cm^{-2}. Comparison of these data with those obtained for the BDD/Pt cell under the same conditions (Fig. 4A) corroborates the existence of a slightly quicker destruction of the drug in the BDD/air-diffusion cell. Thus, at 60 min of electro-oxidation of the synthetic solution the paracetamol decay increased from 43% for the BDD/Pt cell (Fig. 4A) to 57% for the BDD/air-diffusion cell (Fig. 4B). The drug abatement was more enhanced in the real water matrix, although in both cells the time needed for its total removal was same (60 min as seen in Fig. 4A and B). These results evidence the low oxidation power of H_2O_2 and $HO_2^{\bullet}$ to destroy paracetamol, thereby confirming that BDD($^{\bullet}$OH) is the main ROS in the electro-oxidation process.

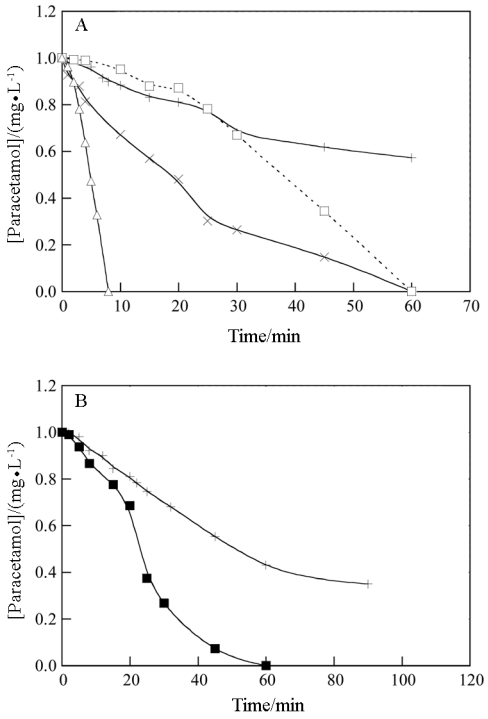

Fig. 4 Change of paracetamol concentration with electrolysis time upon electro-oxidation of 100 mL pharmaceutical mixtures containing 1 mg·L^{-1} of this drug and 1 mg·L^{-1} salicylic acid at pH 3.0 and 25 ℃ (In plot A, BDD/Pt cell: Ultrapure water with 0.05 mol·L^{-1} Na_2SO_4 at (+) 10 mA·cm^{-2} and (×) 50 mA·cm^{-2}; real water matrix at (□) 10 mA·cm^{-2} and (△) 50 mA·cm^{-2}. In plot B, BDD/air-diffusion cell at 10 mA·cm^{-2} : (+) Ultrapure water with 0.05 mol·L^{-1} Na_2SO_4, and (■) real water matrix)

2.4 Electro–Fenton Treatment

The performance of the electro-Fenton process was assessed by adding 0.15 mmol·L^{-1} Fe^{2+} to the solutions of pH 3.0 degraded in the BDD/air-diffusion

cell. The destruction of 1 mg·L^{-1} paracetamol in the real water matrix up to overall disappearance after 60 min at 10 mA·cm^{-2} is shown in Fig. 5. Surprisingly, the removal rate of this drug by electro-Fenton was only slightly higher than that found by electro-oxidation at 10 mA·cm^{-2} (Fig. 2), in contrast to previous work[25-26] where the former method showed a much higher efficiency owing to the significantly faster reaction of paracetamol with homogeneous •OH formed from Fenton's reaction (3) than with BDD(•OH) in 0.05 mol·L^{-1} Na_2SO_4. This phenomenon can be mainly explained by the inhibitory effect of Cl^- presented in the real water matrix on generated •OH, giving rise to weak active chlorine species like $ClOH^{\bullet-}$, $Cl^\bullet$, $Cl_2^{\bullet-}$, and $Cl_{2(g)}$ via the following reactions[45-46]:

$$^\bullet OH + Cl^- \leftrightarrow ClOH^{\bullet-} \quad (17)$$

$$ClOH^{\bullet-} + H^+ \rightarrow Cl^\bullet + H_2O \quad (18)$$

$$ClOH^{\bullet-} + Cl^- \rightarrow Cl_2^{\bullet-} + OH^- \quad (19)$$

$$Cl^\bullet + Cl^- \leftrightarrow Cl_2^{\bullet-} \quad (20)$$

$$2Cl_2^{\bullet-} \rightarrow Cl_{2(g)} + 2Cl^- \quad (21)$$

The inhibition by Cl^- was confirmed from the similar paracetamol decay found for a drug mixture in synthetic and real solutions, as shown in Fig. 5. The enhancement of drug removal observed for its electro-oxidation in the real water matrix in Fig. 4 ascribed to the parallel action of active chlorine species was not produced in electro-Fenton because of the destruction of •OH with Cl^-. The presence of Cl^- in the real water matrix is then beneficial to increase the oxidation power of electro-oxidation, but clearly detrimental for electro-Fenton since it reduces its oxidation ability.

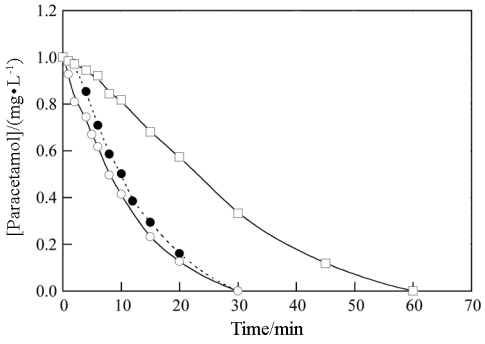

Fig. 5 Removal of paracetamol with electrolysis time for the electro-Fenton treatment of 100 mL of 1 mg·L^{-1} pharmaceutical solutions with 0.15 mmol·L^{-1} Fe^{2+} of pH 3.0 and 25 ℃ in a BDD/air-diffusion cell at 10 mA·cm^{-2} (Paracetamol alone: (□) Real water matrix. Paracetamol in a mixture with 1 mg·L^{-1} salicylic acid: (●) Ultrapure water with 0.05 mol·L^{-1} Na_2SO_4, and (○) real water matrix)

2.5 DOC Decay and Evolution of Oxidation By-Products in the Real Water Matrix

In natural and engineered systems, the reactivity between NOM and some oxidants such as •OH is of great importance since these natural organic compounds may act as radical scavengers, therefore altering the performance of the AOPs[47]. The change of DOC with time for those trials shown above that were performed in real water matrix was determined to assess the degree in mineralization of its organic pollutants by the EAOPs tested. The initial DOC of 8.0 mg·L^{-1} for the real water (Tab. 1) was increased to about 8.6 mg·L^{-1} for the single drug solutions and to ca. 9.3 mg·L^{-1} for the multicomponent solutions. The results obtained for selected experiments are depicted in Fig. 6. As can be seen, the use of 10 mA·cm^{-2} in electro-oxidation yielded a very poor mineralization, reaching 15% of DOC decay at 180 min as a consequence of the low amounts of BDD(•OH) and active chlorine species produced at this low j. The mineralization rate of the polluted water was slightly enhanced by means of electro-Fenton, which only attained 23% DOC reduction after being electrolyzed for 180 min at 10 mA·cm^{-2} and 51% DOC removal after the application of 50 mA·cm^{-2} for 120 min (Fig. 6). The slightly better oxidation ability of electro-Fenton compared to electro-oxidation is due to the parallel destruction of organics with •OH although its production from Fenton's reaction (3) is partially inhibited by Cl^-, as stated above. In contrast, Fig. 6 shows that at 50 mA·cm^{-2} a high mineralization degree was already reached in electro-oxidation, being near 90% at 240 min of electrolysis, and even 95% at 180 min by the addition of 0.05 mol·L^{-1} Na_2SO_4 probably due to the additional oxidation of pollutants by the larger quantities of $S_2O_8^{2-}$ formed from Reaction (14). High j

values and high contents of Cl^- and SO_4^{2-} are then key factors to obtain an almost total mineralization of the dissolved NOM in the real water matrix upon electro-oxidation.

Reversed-phase HPLC analysis of single paracetamol solutions treated by electro-oxidation revealed the formation of traces of *p*-benzoquinone (< 0.2 mg·L^{-1}), which persisted for long time, for example, up to 240 min at 50 mA·cm^{-2}. This derivative can arise from the oxidation of hydroquinone, which is formed from the paracetamol hydroxylation with cleavage of the C(1)—N bond[11]. On the other hand, ion chromatograms of all treated paracetamol solutions exhibited traces of NO_3^- and NH_4^+ ions, presumably produced from the drug degradation[11, 26] because the TN measured for the trials with the real water matrix did not vary with electrolysis time. This indicates that N-compounds contained in the real water matrix are very recalcitrant since they are destroyed by neither hydroxyl radicals nor active chlorine species generated in electro-oxidation and electro-Fenton.

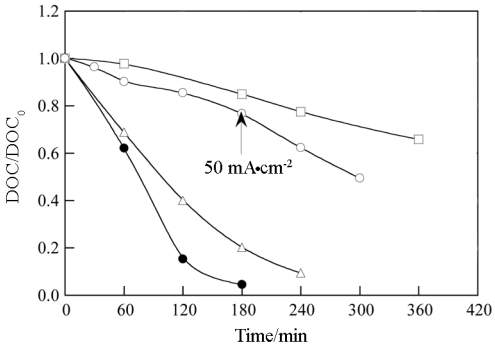

Fig. 6 Normalized DOC decay vs. electrolysis time for 100 mL real water matrix at pH 3.0 and 25 ℃ (□, △, ●) 1 mg·L^{-1} paracetamol, by electro-oxidation; (○) 1 mg·L^{-1} paracetamol + 1 mg·L^{-1} salicylic acid, by electro-Fenton. Applied current density: (□, ○) 10 mA·cm^{-2} and (△, ●) 50 mA·cm^{-2}. (●) In the presence of 0.05 mol·L^{-1} Na_2SO_4

3 Conclusions

It has been demonstrated that 1 mg·L^{-1} paracetamol and/or 1 mg·L^{-1} salicylic acid contained in a real water matrix at pH 3.0 are destroyed by electro-oxidation with a BDD anode. Their decay is faster in this medium than in a synthetic solution with 0.05 mol·L^{-1} Na_2SO_4 due to their favored reaction in the bulk with highly oxidizing active chlorine species produced from the oxidation of Cl^- ion. The increase in *j* from 10 to 50 mA·cm^{-2} causes a large enhancement in the removal of both compounds, which disappear in about 5 min, as a result of the high production of oxidants. This behavior also occurs using the real water mixture at natural alkaline pH. When the drug mixture is treated, the competitive attack of generated oxidants over them decelerates their abatement. Comparative assays with BDD/Pt and BDD/air-diffusion cells have shown a very low oxidation ability of other ROS like H_2O_2 and $HO_2^{\bullet}$ in comparison to BDD ($^{\bullet}OH$) in electro-oxidation. Furthermore, only a slight acceleration of drug removal has been found in the real water matrix using electro-Fenton with a BDD anode, owe to the partial destruction of homogeneous $^{\bullet}OH$ formed from Fenton's reaction (3) with Cl^-. High mineralization degrees can be reached at a high *j* of 50 mA·cm^{-2}, attaining an almost total mineralization with 95% DOC (mainly coming from NOM) reduction for the real water matrix with 1 mg·L^{-1} paracetamol and 0.05 mol·L^{-1} Na_2SO_4 after 180 min of electro-oxidation. Traces of *p*-benzoquinone as well as NO_3^- and NH_4^+ ions have been detected during the electro-oxidation of single paracetamol solutions. However, the TN of the real water matrix is not reduced in none of the trials, which suggests that its N-compounds remain stable upon treatment by these EAOPs under the present conditions.

Acknowledgements: The authors thank the financial support from Ministerio de Ciencia e Innovación, Spain (MICINN) through project CTQ2010-16164/BQU co-financed with FEDER funds.

References:

[1] Kümmerer K. The presence of pharmaceuticals in the environment due to human use - present knowledge and future challenges[J]. Journal of Environmental Management, 2009, 90(8): 2354-2366.

[2] Esplugas S, Bila D M, Krause LGT, et al. Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and per-

sonal care products (PPCPs) in water effluents[J]. Journal of Hazardous Materials, 2007, 149(3): 631-642.

[3] Sirés I, Brillas E. Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review[J]. Environment International, 2012, 40: 212-229.

[4] Jones OAH, Voulvoulis N, Lester J N. Human pharmaceuticals in wastewater treatment processes[J]. Critical Reviews in Environmental Science and Technology, 2005, 35(4): 401-427.

[5] Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes[J]. Environment International, 2009, 35(2): 402-417.

[6] Rahman M F, Yanful E K, Jasim S Y. Occurrences of endocrine disrupting compounds and pharmaceuticals in the aquatic environment and their removal from drinking water: Challenges in the context of the developing world[J]. Desalination, 2009, 248(1/3): 578-585.

[7] Panizza M, Cerisola G. Direct and mediated anodic oxidation of organic pollutants[J]. Chemical Reviews, 2009, 109 (12): 6541-6569.

[8] Brillas E, Sirés I, Oturan M A. Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry[J]. Chemical Reviews, 2009, 109(12): 6570-6631.

[9] Özcan A, Şahin Y, Koparal A S, et al. Propham mineralization in aqueous medium by anodic oxidation using boron-doped diamond anode: Influence of experimental parameters on degradation kinetics and mineralization efficiency[J]. Water Research, 2008, 42(12): 2889-2898.

[10] Marselli B, Garcia-Gomez J, Michaud P A, et al. Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes[J]. Journal of The Electrochemical Society, 2003, 150(3): D79-D83.

[11] Brillas E, Sirés I, Arias C, et al. Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode[J]. Chemosphere, 2005, 58(4): 399-406.

[12] Liu L, Zhao G H, Wu M F, et al. Electrochemical degradation of chlorobenzene on boron-doped diamond and platinum electrodes[J]. Journal of Hazardous Materials, 2009, 168(1): 179-186.

[13] Santos V, Diogo J, Pacheco M J A, et al. Electrochemical degradation of sulfonated amines on Si/BDD electrodes [J]. Chemosphere, 2010, 79(6): 637-645.

[14] Cañizares P, García-Gómez J, Lobato J, et al. Electrochemical oxidation of aqueous carboxylic acid wastes using diamond thin-film electrodes[J]. Industrial & Engineering Chemistry Research, 2003, 42(5): 956-962.

[15] Cañizares P, Paz R, Sáez C, et al. Electrochemical oxidation of alcohols and carboxylic acids with diamond anodes: A comparison with other advanced oxidation processes[J]. Electrochimica Acta, 2008, 53(5): 2144-2153.

[16] Sirés I, Brillas E, Cerisola G, et al. Comparative depollution of mecoprop aqueous solutions by electrochemical incineration using BDD and PbO_2 as high oxidation power anodes[J]. Journal of Electroanalytical Chemistry, 2008, 613(2): 151-159.

[17] Sirés I, Oturan N, Oturan M A, et al. Electro-Fenton degradation of antimicrobials triclosan and triclocarban [J]. Electrochimica Acta, 2007, 52(17): 5493-5503.

[18] Sirés I, Garrido J A, Rodríguez R M, et al. Catalytic behavior of the Fe^{3+}/Fe^{2+} system in the electro-Fenton degradation of the antimicrobial chlorophene[J]. Applied-Catalysis B: Environmental, 2007, 72(3/4): 382-394.

[19] Oturan N, Panizza M, Oturan M A. Cold incineration of chlorophenols in aqueous solution by advanced electrochemical process electro-Fenton. Effect of number and position of chlorine atoms on the degradation kinetics[J]. The Journal of Physical Chemistry A, 2009, 113 (41): 10988-10993.

[20] Sirés I, Oturan N, Oturan M A. Electrochemical degradation of β-blockers. Studies on single and multicomponent synthetic aqueous solutions[J]. Water Research, 2010, 44 (10): 3109-3120.

[21] Oturan M A, Oturan N, Edelahi M C, et al. Oxidative degradation of herbicide diuron in aqueous medium by Fenton's reaction based advanced oxidation processes[J]. Chemical Engineering Journal, 2011, 171(1): 127-135.

[22] Oturan N, Brillas E, Oturan M A. Unprecedented total mineralization of atrazine and cyanuric acid by anodic oxidation and electro-Fenton with a boron-doped diamond anode[J]. Environmental Chemistry Letters, 2012, 10(2): 165-170.

[23] Sirés I, Centellas F, Garrido J A, et al. Mineralization of

clofibric acid by electrochemical advanced oxidation processes using a boron-doped diamond anode and Fe^{2+} and UVA light as catalysts[J]. Applied Catalysis B: Environmental, 2007, 72(3/4): 373-381.

[24] Skoumal M, Rodríguez R M, Cabot P L, et al. Electro-Fenton, UVA photoelectro-Fenton and solar photoelectro-Fenton degradation of the drug ibuprofen in acid aqueous medium using platinum and boron-doped diamond anodes[J]. Electrochimica Acta, 2009, 54(7): 2077-2085.

[25] Almeida L C, Garcia-Segura S, Bocchi N, et al. Solar photoelectro-Fenton degradation of paracetamol using a flow plant with a Pt/air-diffusion cell coupled with a compound parabolic collector: Process optimization by response surface methodology[J]. Applied Catalysis B: Environmental, 2011, 103(1/2): 21-30.

[26] Sirés I, Garrido J A, Rodríguez R M, et al. Electrochemical degradation of paracetamol from water by catalytic action of Fe^{2+}, Cu^{2+}, and UVA light on electrogenerated hydrogen peroxide [J]. Journal of The Electrochemical Society, 2006, 153(1): D1-D9.

[27] Guinea E, Arias C, Cabot P L, et al. Mineralization of salicylic acid in acidic aqueous medium by electrochemical advanced oxidation processes using platinum and boron-doped diamond as anode and cathodically generated hydrogen peroxide[J]. Water Research, 2008, 42(1/2): 499-511.

[28] Filella M. Freshwaters: Which NOM matters? [J]. Environmental Chemistry Letters, 2009, 7(1): 21-35.

[29] Espinoza L A T, Frimmel F H. A simple simulation of the degradation of natural organic matter in homogeneous and heterogeneous advanced oxidation processes[J]. Water Research, 2009, 43(16): 3902-3909.

[30] Matilainen A, Sillanpää M. Removal of natural organic matter from drinking water by advanced oxidation processes[J]. Chemosphere, 2010, 80(4): 351-365.

[31] Andreozzi R, Caprio V, Marotta R, et al. Paracetamol oxidation from aqueous solutions by means of ozonation and H_2O_2/UV system [J]. Water Research, 2003, 37 (5): 993-1004.

[32] Radjenovic J, Bagastyo A, Rozendal R A, et al. Electrochemical oxidation of trace organic contaminants in reverse osmosis concentrate using RuO_2/IrO_2 coated titanium cathodes [J]. Water Research, 2011, 45 (4): 1579-1586.

[33] Bound JP, Vaulvaulis N. Pharmaceuticals in the aquatic environment - a comparison of risk assessment strategies [J]. Chemosphere, 2004, 56(11): 1143-1155.

[34] Nakada N, Tanishima T, Shinohara H, et al. Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water Research, 2006, 40 (7): 3297-3303.

[35] Waterston K, Wang J W, Bejan D, et al. Electrochemical wastewater treatment: Electrooxidation of acetaminophen [J]. Journal of Applied Electrochemistry, 2006, 36 (2): 227-232.

[36] Matyasovszky N, Tian M, Chen A. Kinetic study of the electrochemical oxidation of salicylic acid and salicylaldehyde using UV/Vis spectroscopy and multivariate cali bration[J]. The Journal of Physical Chemistry A, 2009, 113(33): 9348-9353.

[37] Su C C, Chang A T, Bellotindos L M, et al. Degradation of acetaminophen by Fenton and electro-Fenton processes in aerator reactor[J]. Separation and Purification Technology, 2012, 99: 8-13.

[38] Brillas E, Baños M A, Camps S, et al. Catalytic effect of Fe^{2+}, Cu^{2+}, and UVA light on the electrochemical degradation of nitrobenzene using an oxygen-diffusion cathode [J]. New Journal of Chemistry, 2004, 28(2): 314-322.

[39] Enache T A, Chiorcea-Paquim A M, Fatibello-Filho O, et al. Hydroxyl radicals electrochemically generated in situ on a boron doped diamond electrode[J]. Electrochemistry Communications, 2009, 11(7): 1342-1345.

[40] Polcaro A M, Vacca A, Mascia M, et al. Electrochemical treatment of waters with BDD anodes: Kinetics of the reactions involving chlorides[J]. Journal of Applied Electrochemistry, 2009, 39(11): 2083-2092.

[41] Mascia M, Vacca A, Polcaro A M, et al. Electrochemical treatment of phenolic waters in presence of chloride with boron-doped diamond (BDD) anodes: Experimental study and mathematical model[J]. Journal of Hazardous Materials, 2010, 174(1/3): 314-322.

[42] Boxall C, Kelsall G H. Hypochlorite electrogeneration. II. Thermodynamics and kinetic model of the anode reaction layer[J]. Institution of Chemical Engineers Symosium Se-

ries, 1992, 127: 59-70.

[43] Bergmann M E H, Rollin J, Iourtchouk T. The occurrence of perchlorate during drinking water electrolysis using BDD anodes[J]. Electrochimica Acta, 2009, 54(7): 2102-2107.

[44] Randazzo S, Scialdone O, Brillas E, et al. Comparative electrochemical treatments of two chlorinated aliphatic hydrocarbons. Time course of the main reaction by-products[J]. Journal of Hazardous Materials, 2011, 192(3): 1555-1564.

[45] De Laat J, Le G T, Legube B. A comparative study of the effects of chloride, sulfate, and nitrate ions on the rates of decomposition of H_2O_2 and organic compounds by Fe(II)/H_2O_2 and Fe(III)/H_2O_2[J]. Chemosphere, 2004, 55(5): 715-723.

[46] Grebel J E, Pignatello J J, Mitch W A. Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters[J]. Environmental Science & Technology, 2010, 44(17): 6822-6828.

[47] McKay G, Dong M M, Kleinman J L, et al. Temperature dependence of the reaction between the hydroxyl radical and organic matter[J]. Environmental Science & Technology, 2011, 45(16): 6932-6937.

掺硼金刚石阳极电氧化和电芬顿工艺处理真实水体中低含量药物的研究

Ignasi Sirés, José Antonio Garrido, Enric Brillas*

(*Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès* 1-11, 08028 *Barcelona, Spain*)

摘要: 本文报告了采用掺硼金刚石阳极(BDD)电氧化和电芬顿工艺处理真实水体中注入含有少量药物残留物的单组分和多组分溶液(即 1 mg·L^{-1} 对乙酰氨基酚和(或)1 mg·L^{-1} 水杨酸, pH=3)的研究结果. 以恒定电流密度方式在 BDD/Pt 电解池中进行电氧化,而在 BDD/空气扩散电解池中进行电芬顿,从而在阴极电生 H_2O_2. 结果表明,由于乙酰氨基酚和水杨酸均与溶液中氯离子氧化所产生的活性氯物种发生反应,因此,电氧化处理真实水体中两种药物的降解要比超纯水中添加 0.05 mol·L^{-1} Na_2SO_4 快. 这种含氯氧化剂的反应活性甚至超过了阳极形成的有限的羟基活性基,提高电流密度大大加速了两种污染物的消除. 在真实水体自然碱性 pH 下得到了类似的结果. 当电氧化处理两种药物的混合物时,两种药物上面产生的氧化剂的竞争作用,导致药物的降解变慢,只有电芬顿处理真实水体时药物的降解才稍微加快,这是由于 H_2O_2 与 Cl^- 的反应,生成了反应活性弱得多的含氯活性基,从而抑制了电生的 H_2O_2 和添加的 Fe^{2+} 之间发生的芬顿反应所形成的同相羟基活性基的累积. 对于添加了药物的真实水体,在较高的电流密度下电氧化可得到较好的天然有机物成分(NOM)矿化度,且添加 0.05 mol·L^{-1} Na_2SO_4 效果会更好. 虽然在药物溶液的电氧化中检测出微量的氧化副产物,如对苯醌、NO_3^- 和 NH_4^+ 离子,但在本研究条件下无法去除真实水体中所含有的氮基化合物.

关键词: 掺硼金刚石阳极; 电氧化; 电芬顿; 药物; 真实水体; 水杨酸