**Contribution of cathodic hydroxyl radical generation to the
enhancement of electro-oxidation process for water
decontamination**

Alejandro Medel ^a, José Treviño-Reséndez ^a, Enric Brillas ^{b, #}, Yunny Meas ^{a, #, **},

Ignasi Sirés ^{b, #, *}

^a *Centro de Investigación y Desarrollo Tecnológico en Electroquímica, S. C., Parque
Tecnológico Querétaro-Sanfandila, C. P. 76730, Pedro Escobedo, Estado de Querétaro,
Mexico*

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

*Paper submitted to be published in **Electrochimica Acta***

* Corresponding author: Tel.: +34 934039240.

E-mail address: i.sires@ub.edu (I. Sirés)

** Corresponding author: E-mail address: yunnymeas@cideteq.mx (Y. Meas)

[#]Active ISE member

Abstract

The degradation of organic pollutants in water by electro-oxidation (EO) process is a very active research topic, but it has been pre-eminently focused on the development of anodes with enhanced electrocatalytic ability to produce $\bullet\text{OH}$ at their surface. Conversely, the degradation pathways that may arise from the potential $\bullet\text{OH}$ production at the cathode surface are often disregarded. This work discusses the contribution of $\bullet\text{OH}$, formed at a Ti, graphite, stainless steel or Pt cathode from the reduction of O_2 or H_2O_2 , to phenol oxidation in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ medium. The $\bullet\text{OH}$ production in the cathodic compartment of a divided cell was assessed from coumarin oxidation monitored via UV/Vis spectroscopy and HPLC with a fluorescence detector, salicylic acid oxidation evaluated by HPLC with a photodiode array detector and electron paramagnetic resonance. It was demonstrated that the production depended on the cathode nature, decreasing as: $\text{Pt} > \text{graphite} \gg \text{stainless steel} > \text{Ti}$. It was concluded that a two-electron reaction converted O_2 to H_2O_2 , which was monoelectronically reduced to $\bullet\text{OH}$. The results reveal the importance of cathode selection in water treatment by EO.

Keywords: Boron-doped diamond; Electrochemical oxidation; Electrochemical reduction; Hydroxyl radical; Water treatment

1. Introduction

Growing research is focused on the electro-oxidation (EO) treatment of water contaminated with toxic and recalcitrant organic compounds. These studies have mainly addressed the application of different active and non-active anodes [1–5], with the purpose of synthesizing new materials or improving the performance of existing ones [7–9]. Among tested materials, PbO_2 , Sb-doped SnO_2 and boron-doped diamond (BDD) are preferred over conventional graphite and dimensionally stable anodes (DSA[®]), owing to their greater ability to form different oxidants (O_2 , hydroxyl radical ($\bullet\text{OH}$) and H_2O_2 , among others) from reactions (1)-(3) (see Table 1). The BDD anode has emerged more vigorously due to its outstanding physical and chemical properties as compared with other electrode materials, finding numerous electrochemical applications such as water decontamination [10], electroanalysis of organic compounds and biomolecules [11], and energy conversion [12].

Much less is known about the role of the cathodic material in EO. Four main cases have been considered: (i) evolution of H_2 , (ii) direct reduction of pollutants and their intermediates, (iii) electrodeposition of metals and (iv) indirect production of oxidizing agents. The evolution of H_2 is significant if the cathode possesses a low overpotential for reactions (4) and (5) [7], whereas alternative products appear if the required overpotential is too large [13].

Several authors have reported the reduction of pollutants and their intermediates at the cathode surface during EO. Kötzt et al. [14], using a Pt anode and a Ti/Pt cathode for the EO of phenol solutions, detailed the formation of the benzoquinone/hydroquinone redox system as cathodic by-products. Similarly, Polcaro et al. [15] suggested that intermediates generated during the EO of 2-chlorophenol solutions could be reduced at the cathode. Azzam et al. [7] showed that the cathode nature (Pb, Zn or Cu) and pH affected the kinetics of 4-chlorophenol degradation by EO using a Ti/RuO₂ anode, although such effects were explained in depth. The importance of the cathode in EO has been mentioned recurrently [15–18], but few researchers

have made a rigorous investigation. Recently, Borràs et al. [19] reported the EO of atrazine solutions with a BDD anode, showing that its degradation was favored using a stainless steel (SS)-304 cathode instead of an air-diffusion electrode.

The contamination related with the discharge of industrial wastewater with high content of heavy metals can be remediated by EO, addressing the simultaneous oxidation of organic pollutants and metal electrodeposition [20]. On the other hand, some cathodes are able to produce oxidizing agents. The most exploited process is the reduction of O_2 to H_2O_2 , which is a weak oxidant with potential application to the treatment of contaminated water [7]. Metallic and carbonaceous materials have been evaluated for H_2O_2 electrogeneration, being the latter ones those possessing higher performance [21]. However, the mechanisms for O_2 reduction reaction (ORR) are still under study [22–25], since the selectivity of the materials to produce H_2O_2 clearly shows the effect of the cathode composition.

Lately, the feasible $\bullet OH$ production at the cathode has been investigated, although the information is still limited. This radical is a strong oxidizing species with a high standard redox potential ($E^\circ = +2.8$ V vs SHE) [26]. $\bullet OH$ can destroy most organic pollutants mainly via hydrogen abstraction or electrophilic addition to π systems [27]. The latter kinds of reactions are of great interest because of the straightforward application to several areas such as electrosynthesis [28–30], energy production [31,32] and water treatment [33]. For example, Imamura et al. [34] found that the surface of a 316L stainless steel (SS) cathode irreversibly contaminated with absorbed organics could be reactivated via electrolysis of synthetic H_2O_2 because of the $\bullet OH$ formation from reaction (6) with $k_2 = 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. A divided cell with a Pt anode and KCl as supporting electrolyte was used and $\bullet OH$ was detected by electron paramagnetic resonance (EPR). Later, Choi and Bard [35] confirmed the occurrence of reaction (6) by cyclic voltammetry coupled to chemiluminescence. Bo-Tao et al. [36] assessed the $\bullet OH$ production in the cathodic compartment of a divided cell with an oxygenated

K₂SO₄ solution, a Ti/PbO₂ anode and a SS-304 cathode, by UV/Vis spectroscopy using its reaction with *N,N*-dimethyl-*p*-nitrosoaniline (RNO) as spin trap [37]. However, it is known that analysis with RNO can lead to false positives [38].

Note that the four-electron reduction of O₂ is strictly dependent on pH, generating either hydroxide anion (OH⁻) by reaction (7) with $E^{\circ} = +0.401$ V vs SHE in alkaline medium [39] or water by reaction (8) with $E^{\circ} = +1.229$ V vs SHE under acidic conditions [40]. The two-electron reduction of O₂ to H₂O₂ in acidic medium may be explained by the initial formation of oxygen radical anion (O₂^{•-}) from reaction (9), followed by its reduction via reaction (10) and (11), although no experimental evidence has been presented yet. This mechanism differs from that proposed in alkaline medium, based on the ionization of H₂O₂ to its conjugated base (HO₂⁻) via reaction (13) with pK_a = 11.62 at 298 K [36,41-43], although H₂O₂ can be either hydrolyzed by OH⁻ from reaction (14) or react with HO₂⁻ to generate [•]OH from reaction (15) [41]. In turn, HO₂⁻ can be reduced to OH⁻ from reaction (16) [44] or undergo chemical decomposition to OH⁻ and O₂ from reaction (17). Reaction (18) accounts for the overall reaction in acidic medium, with $E^{\circ} = +0.67$ V vs SHE [45]. This species can then follow various routes: (i) cathodic reduction to water from reaction (19) with $E^{\circ} = +1.776$ V vs SHE [45], (ii) chemical decomposition to water and O₂ by reaction (20) [20,46], (iii) anodic oxidation to O₂ from reaction (21) [46] and (iv) reduction to [•]OH and water following reaction (6). This radical can then be either reduced to water from reaction (22) [36] or react with H₂O₂ yielding hydroperoxyl radical (HO₂[•]) and water from reaction (23) [34], impeding its detection.

The possible [•]OH production in the presence of O₂ has also been reported by Noël et al. [47] using Pt as cathode and coupling two analytical techniques, namely radical footprinting and scanning electrochemical microscopy. Although the authors agreed with the [•]OH generation according to reaction (6), they proposed a new 3-electron route to form this radical by reaction (24) on a Pt surface.

During the EO treatment of organic pollutants with a BDD anode, O_2 and H_2O_2 are formed from reaction (1) and (3), respectively [48]. Hence, the cathodic reduction of these species can be expected, possibly forming $\bullet OH$ that can contribute to the global decontamination process. Based on this assumption, the present work aims to evaluate the effect of the cathode nature on EO process with a BDD anode in acidic medium, allowing the electrochemical reduction of O_2 and H_2O_2 to $\bullet OH$. With this purpose, acidic phenol solutions were electrolyzed using Ti, graphite, SS-304 and Pt as cathodes, and the $\bullet OH$ production was evaluated by UV/Vis spectroscopy, reversed-phase high-performance liquid chromatography (RP-HPLC) coupled to a fluorescence detector or a photodiode array and EPR.

2. Experimental

2.1. Chemicals

Sulfuric acid, hydrochloric acid, sodium hydroxide, phenol, coumarin ($C_9H_6O_2$), 7-hydroxycoumarin ($C_9H_6O_3$), *tert*-butanol, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), salicylic acid, 2,5-dihydroxybenzoic acid and 2,3-dihydroxybenzoic acid were purchased from Sigma-Aldrich. Sodium sulfate, used as supporting electrolyte, was purchased from Fluka. Citric and acetic acids were purchased from Merck. HPLC-grade acetonitrile and methanol were from Panreac. High-purity Millipore Milli-Q water (resistivity $> 18.2\text{ M}\Omega\text{ cm}$) was employed to prepare all solutions.

2.2. Analytical techniques

The solution pH was measured with a Crison 2000 device, being maintained at 298 K with a Julabo heat exchanger. Potentiodynamic analysis by cyclic voltammetry and linear sweep voltammetry, as well as the electrolyses of phenol solutions, were made using an Autolab PGSTAT 30. Phenol degradation was monitored by UV/Vis spectroscopy using a Lambda XLX'+ spectrophotometer coupled to a flow cell with a Cole Palmer peristaltic pump. All

experiments were performed at 298 K maintained with a Polyscience heat exchanger. During the electrolysis, solutions were vigorously stirred with a magnetic stirrer at 300 rpm. In the electrolytes with O₂ and/or H₂O₂, an Amel 2053 potentiostat-galvanostat was used to establish the cathodic potential (E_{cath}). Total organic carbon (TOC) of solutions was measured on a Shimadzu VCSN TOC analyzer.

The production of •OH and H₂O₂ was analyzed by UV/Vis spectroscopy using a Shimadzu UV-1800 spectrophotometer with temperature set at 298 K with a Polyscience heat exchanger. Indirect analysis of •OH generation through RP-HPLC was made with: (i) a Shimadzu 10Avp LC, fitted with a Thermo Electron Corporation Hypersil ODS 5 μm, 150 mm × 3 mm (i.d.), column at 298 K, and coupled to a Shimadzu RF-10AxL fluorescence detector, and (ii) a Waters 600 LC, fitted with the above column at 308 K, and coupled to a Waters 996 photodiode array detector. •OH detection by EPR was made using a Bruker ESP 300E EPR spectrometer with Win-EPR 2.3 Symphony software. Total Fe was obtained by inductively coupled plasma (ICP) with a Perkin Elmer Optimum 3200 RL equipment.

2.3. Methods

2.3.1. Selection of the reaction media

Polycrystalline BDD (B content of 1300 ppm) thin film of 3 μm thickness, deposited on titanium substrate (Ti/BDD) by hot filament chemical vapor deposition (HF-CVD), was provided by NeoCoat[®]. Before use, this electrode was properly activated (i.e., removal of C-sp² impurities) and cleaned in 0.5 M H₂SO₄ for 15 min by applying a potential of +2.3 V vs Hg/Hg₂SO₄ (K₂SO₄ (sat)) [49,50]. The electrochemical behavior of Ti/BDD in different reaction media was analyzed by cyclic voltammetry, using a conventional three-electrode cell with 60 cm³ capacity. The working electrode was a 2.185 cm² BDD thin film, the counter electrode was a Pt mesh or Ti bar (yielding the same results), and Hg/Hg₂SO₄ (K₂SO₄ (sat)) with $E^{\circ} = +0.640$ V vs SHE was used as reference electrode. Cyclic voltammograms were

recorded with 50 cm³ of 0.5 mol dm⁻³ supporting electrolyte at 298 K, at a scan rate of 100 mV s⁻¹. Prior to each measurement, the solution was deoxygenated with N₂ for 10 min, maintaining the gas flow during the trials.

2.3.2. Selection of phenol concentration

The electrochemical response of Ti/BDD previously activated was assessed by cyclic voltammetry on a wide range of phenol concentrations up to 550 mg dm⁻³. For this analysis, phenol was successively added to a fixed reaction volume (50 cm³ of 0.5 mol dm⁻³ H₂SO₄) until reaching the required concentration. The experimental system and operation conditions were those reported in subsection 2.3.1, but replacing the Pt mesh by a Ti bar. After the evaluation of each potential zone, the Ti/BDD electrode was reactivated in 0.5 mol dm⁻³ H₂SO₄ with a Pt mesh as counter electrode by applying a potential pulse of +2.3 V vs Hg/Hg₂SO₄ for 60 s.

2.3.3. Effect of the cathodic material on the electrochemical reduction of O₂

The electrochemical behavior of Ti, graphite, SS-304 and Pt as the working electrode was studied in 0.5 mol dm⁻³ H₂SO₄ by linear sweep voltammetry. The geometrically active area of each electrode with cylindrical configuration was of 0.1011 cm². The same experimental and operational conditions mentioned in subsection 2.3.2 were utilized. Ti, graphite and SS-304 were sonicated for 10 min before analysis, whereas Pt was flame-annealed followed by electrochemical cleaning. The gap between the working and counter electrodes was 1 mm.

2.3.3.1. Phenol electrolysis

The degradation of phenol was carried out in potentiostatic mode using a 2.185 cm² Ti/BDD anode, a Ti, graphite, SS-304 or Pt cathode and a Hg|Hg₂SO₄ (K₂SO₄ (sat)) as the reference electrode. Solutions of 50 cm³ of 0.5 mol dm⁻³ H₂SO₄ containing 0.320 mmol dm⁻³ phenol (23.0 mg dm⁻³ TOC) were electrolyzed under constant stirring at 300 rpm at an anodic potential $E_{an} = +2.3$ V vs Hg|Hg₂SO₄ for 30 min. Before and after all trials, the electrode

materials were cleaned and reactivated as described above. Phenol removal was monitored by UV/Vis spectroscopy coupling the spectrophotometer to a flow cell where the electrolyzed solution was circulated at $12.5 \text{ cm}^3 \text{ min}^{-1}$. In each electrolysis, samples were withdrawn times for TOC analysis.

2.3.3.2. $\bullet\text{OH}$ production from electrochemical reduction of O_2 and H_2O_2

Solutions of 10 cm^3 of $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at pH 3 adjusted with $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, either saturated with O_2 for 30 min or containing $100 \text{ mmol dm}^{-3} \text{ H}_2\text{O}_2$ with deoxygenation using N_2 , were electrolyzed in the presence of the different probe compounds selected for reacting specifically with generated $\bullet\text{OH}$. The content of this radical was determined by UV/Vis spectroscopy, RP-HPLC coupled to a fluorescence or a photodiode array detector and EPR.

Electrolyses were performed in potentiostatic mode in a three-electrode divided cell of 15 cm^3 capacity containing the above Ti, graphite, SS-304 or Pt electrode as the cathode and a Pt wire as the anode, employing Ag|AgCl (KCl (sat)) as the reference electrode. The Pt wire was placed in the anodic compartment, separated by a Nafion[®] 117 cation exchange membrane, which was previously activated to facilitate the passage of protons and avoid false positives derived from anodic reactions. E_{cath} values between -0.305 and -0.405 V vs Ag|AgCl were selected and the trials were performed under constant stirring at 298 K . All the electrodes were first activated following the protocols detailed above and, between two consecutive tests, they were sonicated for 10 min followed by rinsing with Milli Q water.

For the analysis by UV/Vis spectroscopy, electrolyses were performed by adding coumarin at a concentration of 0.1 mmol dm^{-3} to the $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution of pH 3 and the change of absorbance at $\lambda = 278 \text{ nm}$ was measured for 15 h. Analysis in the presence of $0.05 \text{ mol dm}^{-3} \text{ tert-butanol}$ was additionally made. The electrolyzed solutions in the presence of coumarin were also analyzed by RP-HPLC coupled to a fluorescence detector in order to detect the hydroxylated derivative 7-hydroxycoumarin. The excitation and emission wavelengths

were 314 and 471 nm, respectively, the mobile phase was a 30:70 (v/v) acetonitrile/water mixture at a flow rate of $0.5 \text{ cm}^3 \text{ min}^{-1}$, and its retention time was 2.874 min.

For RP-HPLC analysis with a photodiode array detector, the $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution at pH 3 was electrolyzed after adding salicylic acid at 5 mmol dm^{-3} . The disappearance of salicylic acid and its reaction products (2,3- and 2,5-dihydroxybenzoic acids) was analyzed from the corresponding calibration curves. The separation process was performed isocratically with a mobile phase composed of a mixture of 10% acetonitrile, 10% methanol, 0.03 mol dm^{-3} citric acid, 0.3 mol dm^{-3} acetic acid and water, circulated at $0.5 \text{ cm}^3 \text{ min}^{-1}$. The retention time was 10.0 min for salicylic acid ($\lambda = 301 \text{ nm}$), 5.0 min for 2,3-dihydroxybenzoic acid ($\lambda = 315 \text{ nm}$) and 4.1 min for 2,5-dihydroxybenzoic acid ($\lambda = 330 \text{ nm}$).

Solutions of $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at pH 3 containing $10 \text{ mmol dm}^{-3} \text{ DMPO}$ were electrolyzed under the same conditions and analyzed by EPR employing the following conditions: frequency of 100 kHz, modulation amplitude of 1.429 G, magnetic field center at 3470 G, sweep width of 100 G, time constant of 10.240 ms, sweep time of 83.886 s, microwave frequency of 9.78 GHz and microwave power of 1.997 mW.

The H_2O_2 concentration was determined via the Ti(IV) oxysulfate method [51]. Total Fe measurements through ICP were made in triplicate, with a limit of detection (LOD) $< 5 \text{ ppb}$.

3. Results and Discussion

3.1. Selection of the reaction medium

Phenolic industrial wastewater such as that discharged from refineries or spent caustic contains anions like SO_4^{2-} , Cl^- and OH^- , among others [52]. These ions may have influence on both, the oxidative pathways during phenol degradation and the electrochemical response of a Ti/BDD anode. For this reason, $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, HCl or NaOH solutions were selected as reaction media to clarify the electrochemical behavior of this electrode. Fig. 1 depicts the cyclic

voltammograms obtained at 100 mV s^{-1} . It can be observed that the OER (oxygen evolution reaction) started at about $+1.6 \text{ V}$ in $0.5 \text{ mol dm}^{-3} \text{ NaOH}$ (see Fig. 1c), much earlier than $+2.0$ and $+1.8 \text{ V}$ observed in H_2SO_4 (see Fig. 1a) and HCl (see Fig. 1b), respectively. The lower O_2 -evolution overpotential in NaOH agrees with the expected dependence of the thermodynamic potential values with pH [16]. In practice, alkaline pH can cause the following complications: (i) low current efficiencies for phenol oxidation due to concomitant O_2 evolution, and (ii) formation of scavengers of $\bullet\text{OH}$ such as hydrogen carbonate by reaction (25) and carbonate by reaction (26). The attack of $\bullet\text{OH}$ on carbonate via reaction (27) with $k_2 = 2.8 \times 10^8 - 3.9 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and hydrogen carbonate via reaction (28) with $k_2 = 5.7 \times 10^6 - 8.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [53] decreases its availability for decontamination [54]. Accordingly, alkaline medium was discarded in the present work.

When comparing the profiles of Fig. 1a and b, a largest potential window can be observed using the H_2SO_4 medium. The oxidative differences in such acidic media arise from the production of other oxidizing species like peroxodisulfate in H_2SO_4 and active chlorine in HCl , whose formation reactions compete with water oxidation from reaction (2). It can then be assumed that the different O_2 -evolution overpotentials in these media could have a significant impact on the formation of said species. In earlier work [55], the much superior $\bullet\text{OH}$ production in H_2SO_4 as compared to HCl has been reported and hence, the former acid was selected for subsequent trials.

3.2. Selection of phenol concentration

A discharge with high organic load not only entails a longer electrochemical treatment, but it can also have influence on the electrochemical performance of the Ti/BDD anode. Phenol concentration in industrial phenolic waste can vary between $2,000$ and $11,000 \text{ mg dm}^{-3}$, attaining more than $100,000 \text{ mg dm}^{-3}$ in terms of chemical oxygen demand [52,55]. To evaluate the electroactivity of phenol at the Ti/BDD surface in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, a cyclic

voltammetric study was made considering two potential regions. The stability region was from 0 to +1.4 V vs Hg|Hg₂SO₄, whereas the medium decomposition occurred within the region from +1.4 to +2.8 V vs Hg|Hg₂SO₄. Phenol concentration ranges investigated were 0-140 mg dm⁻³ and 150-550 mg dm⁻³, respectively. No higher phenol contents were considered, in order to prevent the passivation of the Ti/BDD working electrode upon formation of a polymeric film. The cyclic voltammograms recorded in the stability region at 100 mV s⁻¹ are presented in Fig. 2. A clearly irreversible oxidation peak, resulting from the charge transfer during the oxidation of phenol at the Ti/BDD surface, can be seen at an anodic potential (E_p^a) near +1.1 V vs Hg|Hg₂SO₄ at 20 mg dm⁻³ phenol. This peak was shifted to more positive potentials as the substrate content was increased, attaining an E_p^a close to +1.3 V vs Hg|Hg₂SO₄ at 60 mg dm⁻³ phenol. At higher concentration, no oxidation peak could be identified. This behavior can be attributed to the formation of a polymeric film during the oxidation process. Its strong adhesion to the Ti/BDD surface caused the inhibition of charge transfer upon blockage of active sites [56]. In order to clarify the effect of phenol concentration, similar cyclic voltammograms were recorded comprising both regions, i.e., between -1.9 and +2.8 V vs Hg|Hg₂SO₄, with special interest in the range from +1.4 to +2.8 V. The j - E profiles recorded are shown in Fig. 3, showing no significant changes as the phenol content was varied, except for a slight increase in j . This means that phenol was oxidized pre-eminently upon the action of •OH formed from reaction (2), which allows concluding that a quite reproducible oxidative behavior can be expected regardless of the phenol concentration.

3.3. Assessment of the cathodic materials for the electrochemical reduction of O₂ and H₂O₂

In the present work, Ti, graphite, SS-304 and Pt were selected as cathodes due to their electrocatalytic and mechanical properties. As stated in the Introduction, the nature of the cathode affects the type of reduction because of the different H₂ evolution overpotential, eventually modifying the global oxidation process. A first analysis by linear sweep voltammetry

was performed in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ using each cathode. This study showed that water reduction started at an E_{cath} of -0.805, -0.355, -0.305 and -0.305 V vs Ag|AgCl using graphite, SS-304, Ti and Pt, respectively, whereas the corresponding water oxidation was initiated at an E_{an} of +1.145, +0.795, +0.845 and +1.145 V vs Ag|AgCl. This means that only graphite presented a large overpotential for H_2 evolution, being the best cathode for ORR with H_2O_2 electrogeneration.

3.3.1. Phenol electrolysis

To assess the overall influence that the nature of the cathodic material exerts on phenol degradation by EO with a Ti/BDD anode, a solution with 23 mg dm^{-3} TOC of this pollutant in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ was electrolyzed in an undivided cell by applying an $E_{\text{an}} = +2.3 \text{ V}$ vs Hg|Hg₂SO₄. Fig. 4 shows the online UV/Vis analysis of phenol solution at time zero and at 30 min of electrolysis using each of the four cathodes. It can be observed that phenol ($\lambda_{\text{max}} = 270 \text{ nm}$) was transformed into 1,4-benzoquinone ($\lambda_{\text{max}} = 248 \text{ nm}$). By comparing the different absorption spectra, one can conclude that 1,4-benzoquinone was largely accumulated in the sequence: SS-304 > Ti > graphite as the cathode, being absent during the EO with Pt. This trend differs from that pointed out above from the linear sweep voltammetric analysis, where all the cathodes behaved similarly except graphite. Classically, the formation of 1,4-benzoquinone would be explained through the addition of $\bullet\text{OH}$ on the aromatic ring of phenol at the Ti/BDD surface, thereby yielding a dihydroxylated derivative like hydroquinone [56]. Although this intermediate was not detected in the above tests, its formation during phenol electrolysis has been widely documented [56,57]. The 1,4-benzoquinone/hydroquinone couple is a well-known redox pair in equilibrium in aqueous solution [57]. The following considerations can be taken into account: (i) the source of $\bullet\text{OH}$ at the Ti/BDD surface is constant; (ii) 1,4-benzoquinone is formed upon oxidation of hydroquinone, previously generated by oxidation of phenol via $\bullet\text{OH}$ attack [56], with $k_2 = 1.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [58]; and (iii) 1,4-benzoquinone can only be

destroyed through the action of $\bullet\text{OH}$ [57], with $k_2 = 1.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [58]. From this, at a constant E_{an} , one would expect a similar accumulation of 1,4-benzoquinone. The dependence with the cathode employed could then be explained by an additional source of oxidation, acting in concomitance with anodic $\bullet\text{OH}$. This was confirmed from the TOC decay found after 30 min of electrolysis, which was higher using Pt (16%) than the other cathodes (oscillating around 9%). The enhancement of phenol mineralization suggest the generation of a larger amount of oxidizing species in the cell with Pt cathode.

3.3.2. Effect of the counter electrode on $\bullet\text{OH}$ production

3.3.2.1. Electrochemical reduction of O_2

To evidence the possible formation of $\bullet\text{OH}$ from cathodic O_2 reduction, as well as the influence of the material, four analytical techniques were used, namely UV spectroscopy, RP-HPLC coupled to a fluorescence or a photodiode array detector and EPR. It must be considered that, unlike other reactive oxygen species such as H_2O_2 and $\text{HO}_2\bullet$, $\bullet\text{OH}$ has a very limited lifetime (10^{-9} s) [59].

The UV analysis was performed using coumarin as the probe compound. Coumarin is not electroactive in the stability zone [60], and it reacts with $\bullet\text{OH}$ according to reaction (29) with $k_2 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [61], yielding the fluorescent derivative 7-hydroxycoumarin. First, 10 cm^3 of a $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution containing coumarin at 0.1 mmol dm^{-3} were electrolyzed in the cathodic compartment of a divided cell with a Pt cathode by applying an $E_{\text{cath}} = -0.305 \text{ V}$ vs $\text{Ag}|\text{AgCl}$ for 15 h, in the presence of dissolved atmospheric O_2 . Fig. 5a highlights a slight decrease in the absorbance of coumarin at $\lambda_{\text{max}} = 278 \text{ nm}$ along the electrolysis, suggesting a weak generation of oxidants at the cathode. This trend was compared with those using the other cathodes and, as depicted in Fig. 5b, the absorbance decrease was greater using Pt, followed by graphite, SS-304 and Ti, although with an insignificant difference

among the three latter materials. This confirms the greater oxidation ability described above for Pt. A comparative electrolysis was then carried out with an O₂-saturated coumarin solution using this cathode. Fig. 5c shows a remarkable enhancement of coumarin disappearance, which verifies the possible •OH production from O₂ reduction. An analogous trial was made in the presence of *tert*-butanol at a concentration of 0.05 mol dm⁻³, since this compound is a very effective •OH scavenger with $k_2 = 6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [37,62]. Fig. 5c evidences that the initial absorbance of the solution was not reduced in this assay, indicating that all generated •OH reacted with *tert*-butanol [37,62,63], whose concentration was much higher than that of coumarin.

During the electrolysis of the O₂-saturated coumarin solution in 0.05 mol dm⁻³ Na₂SO₄ at pH 3 with each of the four cathodes, 7-hydroxycoumarin formed as product after 15 h at $E_{\text{cath}} = -0.305 \text{ V}$ vs Ag|AgCl was detected by RP-HPLC coupled to a fluorescence detector. Concentrations of 0.27, 0.24, 0.18 and 0.10 μmol dm⁻³ were attained using Pt, graphite, SS-304 and Ti, respectively. These results demonstrate the occurrence of reaction (29), being valid the hypothesis of •OH production in O₂-rich media. Further validation was carried out with Pt and graphite through RP-HPLC analysis with a photodiode array detector. An O₂-saturated 5 mmol dm⁻³ salicylic acid solution with 0.05 mol dm⁻³ Na₂SO₄ at pH 3 was electrolyzed at $E_{\text{cath}} = -0.305 \text{ V}$ vs Ag|AgCl. The acid reacts with •OH with $k_2 = 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [64], yielding a mixture of 2,3- and 2,5-dihydroxybenzoic acids, which can be detected by RP-HPLC. Fig. 6a shows a slow removal of salicylic acid with graphite cathode, being much faster with Pt. The appearance of the two main dihydroxybenzoic acids confirmed the •OH generation with both cathodes. As can be seen in Fig. 6b, 2,5-dihydroxybenzoic acid was the major by-product formed, although both acids were progressively destroyed. Note that only traces of both acids were detected using a Ti or SS-304 cathode.

All the above findings highlight the superior ability of Pt cathode to produce $\bullet\text{OH}$. This was further corroborated by means of EPR based on the $\bullet\text{OH}$ -DMPO adduct signal. Fig. 7 shows the EPR spectra recorded during the treatment of 10 cm³ of an O₂-saturated 10 mmol dm⁻³ DMPO solution with 0.05 mol dm⁻³ Na₂SO₄ at pH 3 in the cathodic compartment of a divided cell with a Pt cathode operating at $E_{\text{cath}} = -0.305 \text{ V vs Ag|AgCl}$. A very weak signal can be observed after 10 min of electrolysis, which was strongly enhanced at 60 min, showing the typical spectrum with four peaks at a relative proportion of 1:2:2:1 related to the adduct. No signals were found in blank experiments involving only the supporting electrolyte, as well as in the presence of 10 mmol dm⁻³ DMPO before current supply. It can also be seen that the typical peaks disappeared in the presence of 0.05 mol dm⁻³ *tert*-butanol, thus confirming the $\bullet\text{OH}$ generation. To validate the EPR results, the conventional Fenton's reaction producing $\bullet\text{OH}$ according to reaction (30) with $k_2 = 63 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [8] was used as a reference pattern. To do this, 10 mmol dm⁻³ H₂O₂ and 1 mmol dm⁻³ Fe²⁺ were added to 10 cm³ of a 10 mmol dm⁻³ DMPO solution with 0.05 mol dm⁻³ Na₂SO₄ at pH 3 and 298 K. Fig. 8 shows the EPR spectrum at 10 min of this trial, which was analogous to spectrum (3) of Fig. 7.

In conclusion, the $\bullet\text{OH}$ production is clearly dependent on the nature of the material used as cathode, as pointed out above, and this could be related either to a monoelectronic reduction of H₂O₂ from reaction (6) or a direct 3-electron O₂ reduction via reaction (24).

3.3.2.2. Analysis of electrogenerated H₂O₂ from O₂ reduction

It has been proposed that in the presence of O₂, H₂O₂ can be formed in acidic medium by global reaction (18), playing an important role in $\bullet\text{OH}$ production from reaction (6) [36,47]. Considering this, the H₂O₂ concentration accumulated in the cathodic compartment of a divided cell containing 10 cm³ of an O₂-saturated 0.05 mol dm⁻³ Na₂SO₄ solution at pH 3 was determined upon electrolysis with the different cathodes at $E_{\text{cath}} = -0.305 \text{ V vs Ag|AgCl}$. The H₂O₂ was quantified using the Ti(IV) oxysulfate method based on reaction (31). Traces of H₂O₂

were determined after 60 min of electrolysis either with graphite (0.0812 mmol dm⁻³) or Pt (0.0810 mmol dm⁻³) cathodes, whereas no H₂O₂ was detected (limit of quantification = 0.05 mmol dm⁻³) using Ti or SS-304. These results are congruent with those about •OH production shown in Fig. 5 and 6, where graphite and Pt were proven as electroactive cathodes. Considering that H₂O₂ can be formed electrochemically through O₂•⁻ according to reactions (9)-(11), or chemically by •OH recombination via reaction (32) with $k_2 = 5.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [62,65], the above solution was electrolyzed again after adding *tert*-butanol at 0.05 mol dm⁻³. As can be seen in Fig. 9, H₂O₂ was detected in the absence and presence of the scavenger, reaching a higher content in the latter case. This phenomenon is apparently contradictory with the expected •OH scavenging effect, as inferred from Fig. 5c and 7, which allows discarding the recombination as main route for H₂O₂ generation. The superior H₂O₂ concentration in the presence of *tert*-butanol suggests that the parasitic reaction (33) with $k_2 = 1.2\text{-}4.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [66] is minimized, thanks to partial •OH destruction. The product, HO₂•, can be either recombined to regenerate H₂O₂ from reaction (34) or be attacked by •OH yielding O₂ and water according to reaction (35) with $k_2 = 1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [65].

Therefore, it can be assumed that the H₂O₂ generated mainly comes from the 2-electron ORR, further being monoelectronically reduced to •OH according to reaction (36). In principle, this allows discarding the proposed 3-electron reduction of O₂ to •OH via reaction (24).

3.3.2.3. Electrochemical reduction of H₂O₂

Aiming to confirm the effect of the cathode on the •OH production in acidic medium from reaction (36), a solution of 10 cm³ containing 0.05 mol dm⁻³ Na₂SO₄, 10 mmol dm⁻³ DMPO and a high H₂O₂ concentration (100 mmol dm⁻³) at pH 3 was put in the cathodic compartment of a divided cell and electrolyzed using each cathodic material at $E_{\text{cath}} = -0.305 \text{ V}$ vs Ag|AgCl, after deoxygenation under a N₂ stream. Fig. 10 shows the EPR spectra obtained after 10 and 60 min of electrolysis using the Pt cathode. As can be seen, the signal corresponding to the •OH-

DMPO adduct was much more intense at 10 min, in agreement with the gradual disappearance of H_2O_2 due to its cathodic electrochemical reduction.

To know the effect of the applied cathodic potential on $\bullet\text{OH}$ generation using Pt, a solution with the same composition of that mentioned above was electrolyzed at E_{cath} values of -0.205, -0.305 and -0.405 V vs Ag|AgCl for 10 min. Similar EPR spectra to that shown in Fig. 10 were recorded in all cases, with a slightly higher signal intensity at $E_{\text{cath}} = -0.405$ V vs Ag|AgCl. This is indicative of a rather insignificant effect of the cathodic potential on the $\bullet\text{OH}$ generation from reaction (36). The same behavior was found with Ti, graphite and SS-304 as alternative cathodes.

Fig. 11 collects the comparative EPR spectra obtained using SS-304, graphite and Ti cathodes for 10 min at $E_{\text{cath}} = -0.305$ V vs Ag|AgCl. Similar spectra can be observed in all cases, accounting for the monoelectronic H_2O_2 reduction to $\bullet\text{OH}$ at each cathode. Taking into account that Fe^{2+} ion is a catalyst that accelerates the decomposition of H_2O_2 to form $\bullet\text{OH}$ via Fenton's reaction (30), ICP analysis of the solution was done to discard false positives. This analysis excluded the presence of Fe^{2+} in the solution since its content was lower than its LOD. From these findings, one can conclude that H_2O_2 can be effectively reduced to generate $\bullet\text{OH}$ and hence, in acidic medium containing O_2 or H_2O_2 , this radical is originated from reaction (36) using a Pt or graphite cathode. If H_2O_2 is not electrogenerated, $\bullet\text{OH}$ is not detected or it is produced at very low concentrations, as observed using SS-304 and Ti as cathodes.

4. Conclusions

This work demonstrates the greater or lower $\bullet\text{OH}$ production in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ medium via electrochemical reduction of O_2 and H_2O_2 at a Ti, graphite, SS-304 and Pt cathode. RP-HPLC coupled to a fluorescence detector revealed the formation of 7-hydroxycoumarin from coumarin hydroxylation, being Pt cathode clearly better to generate $\bullet\text{OH}$. Graphite

cathode also presented a good electroactivity for $\bullet\text{OH}$ production, whereas it was much poorer in the case of SS-304 and Ti. The study on phenol oxidation with a BDD anode in an undivided cell confirmed the above behavior of each cathode. From the addition of H_2O_2 to a DMPO solution, it was established that at pH 3, $\bullet\text{OH}$ was formed from the monoelectronic reduction of H_2O_2 , rather than from the direct 3-electron reduction of O_2 . The ORR occurred via a 2-electron pathway with H_2O_2 as product. These results clarify the contribution of the cathode in the EO process for water treatment, since each material can contribute in a different manner to the global generation of the main oxidant, $\bullet\text{OH}$.

Acknowledgments

The authors acknowledge funding from the Consejo Nacional de Ciencia y Tecnología de los Estados Unidos Mexicanos (CONACYT, Mexico) as well as from project CTQ2016-78616-R (AEI/FEDER, EU). We also thank Yomara Barrera by the revision of this manuscript.

References

- [1] C. Comninellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for wastewater treatment, *Electrochim. Acta.* 39 (1994) 1857–1862.
- [2] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, *Chem. Rev.* 109 (2009) 6541–6569.
- [3] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, Single and coupled electrochemical processes and reactors for the abatement of organic pollutants: A critical review, *Chem. Rev.* 115 (2015) 13362–13407.
- [4] R.A. Herrada, A. Medel, F. Manríquez, I. Sirés, E. Bustos, Preparation of $\text{IrO}_2\text{-Ta}_2\text{O}_5/\text{Ti}$ electrodes by immersion, painting and electrophoretic deposition for the electrochemical removal of hydrocarbons from water, *J. Hazard. Mater.* 319 (2016) 102–110.

- [5] S. Lanzalaco, I. Sirés, A. Galia, M.A. Sabatino, C. Dispenza, O. Scialdone, Facile crosslinking of poly(vinylpyrrolidone) by electro-oxidation with IrO₂-based anode under potentiostatic conditions, *J. Appl. Electrochem.* 48 (2018) 1343–1352.
- [6] M. Zhou, Q. Dai, L. Lei, C. Ma, D. Wang, Long life modified lead dioxide anode for organic wastewater treatment: electrochemical characteristics and degradation mechanism, *Environ. Sci. Technol.* 39 (2005) 363–370.
- [7] M.O. Azzam, Y. Tahboub, M. Al-Tarazi, Effect of counter electrode material on the anodic destruction of 4-Cl phenol solution, *Process Safety Environ. Protection* 77 (1999) 219–226.
- [8] E. Brillas, I. Sirés, M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry, *Chem. Rev.* 109 (2009) 6570–6631.
- [9] G. Ramírez, F.J. Recio, P. Herrasti, C.A. Ponce-de-León, I. Sirés, Effect of RVC porosity on the performance of PbO₂ composite coatings with titanate nanotubes for the electrochemical oxidation of azo dyes, *Electrochim. Acta.* 204 (2016) 9–17.
- [10] Y. He, H. Lin, Z. Guo, W. Zhang, H. Li, W. Huang, Recent developments and advances in boron-doped diamond electrodes for electrochemical oxidation of organic pollutants, *Sep. Purif. Technol.* 212 (2019) 802–821.
- [11] S. Baluchová, A. Daňhel, H. Dejmková, V. Ostatná, K. Schwarzová-Pecková, Recent progress in the applications of boron doped diamond electrodes in electroanalysis of organic compounds and biomolecules - A review, *Anal. Chim. Acta* 1077 (2019) 30–66.
- [12] K.I.B. Eguiluz, J.M. Peralta-Hernández, A. Hernández-Ramírez, J.L. Guzmán-Mar, L. Hinojosa-Reyes, C.A. Martínez-Huitle, G.R. Salazar-Banda, The use of diamond for energy conversion system applications: A review, *Int. J. Electrochem.* 2012 (2012) 20.
- [13] N. Sonoyama, T. Sakata, Electrochemical decomposition of CFC-12 using gas diffusion electrodes, *Environ. Sci. Technol.* 32 (1998) 375–378.

- 477 [14] R. Kötzt, S. Stucki, B. Carcer, Electrochemical waste water treatment using high
478 overvoltage anodes Part II : Anode performance and applications, J. Appl. Electrochem.
479 21 (1991) 99–104.
- 480 [15] A.M. Polcaro, S. Palmas, F. Renoldi, M. Mascia, On the performance of Ti/SnO₂ and
481 Ti/PbO₂ anodes in electrochemical degradation of 2-chlorophenol for wastewater
482 treatment, J. Appl. Electrochem. 29 (1999) 147–151.
- 483 [16] D. Reyter, D. Bélanger, L. Roué, Nitrate removal by a paired electrolysis on copper and
484 Ti/IrO₂ coupled electrodes - Influence of the anode/cathode surface area ratio, Water
485 Res. 44 (2010) 1918–1926.
- 486 [17] A.J. Méndez-Martínez, M.M. Dávila-Jiménez, O. Ornelas-Dávila, M.P. Elizalde-
487 González, U. Arroyo-Abad, I. Sirés, E. Brillas, Electrochemical reduction and oxidation
488 pathways for Reactive Black 5 dye using nickel electrodes in divided and undivided cells,
489 Electrochim. Acta 59 (2012) 140–149.
- 490 [18] R. Oriol, M.P. Bernícola, E. Brillas, P.L. Cabot, I. Sirés, Paired electro-oxidation of
491 insecticide imidacloprid and electrodenitrification in simulated and real water matrices,
492 Electrochim. Acta 317 (2019) 753–765.
- 493 [19] N. Borràs, R. Oliver, C. Arias, E. Brillas, Degradation of atrazine by electrochemical
494 advanced oxidation processes using a boron-doped diamond anode, J. Phys. Chem. A.
495 114 (2010) 6613–6621.
- 496 [20] F.F. Rivera, I. González, J.L. Nava, Chromium-plating industry using a rotating cylinder
497 electrode (RCE) reactor, Environ. Technol. 29 (2008) 817–825.
- 498 [21] Z. Ye, D.R.V. Guelfi, G. Álvarez, F. Alcaide, E. Brillas, I. Sirés, Enhanced
499 electrocatalytic production of H₂O₂ at Co-based air-diffusion cathodes for the
500 photoelectro-Fenton treatment of bronopol, Appl. Catal. B: Environ. 247 (2019) 191–
501 199.

- [22] M. Shao, P. Liu, R.R. Adzic, Superoxide anion is the intermediate in the oxygen reduction reaction on platinum electrodes, *J. Am. Chem. Soc.* 128 (2006) 7408–7409.
- [23] V. Tripkovi, E. Skúlason, S. Siahrostami, J.K. Nørskov, J. Rossmeisl, The oxygen reduction reaction mechanism on Pt (111) from density functional theory calculations, *Electrochim. Acta* 55 (2010) 7975–7981.
- [24] I. Katsounaros, W.B. Schneider, J.C. Meier, U. Benedikt, P.U. Biedermann, A.A. Auer, K.J.J. Mayrhofer, Hydrogen peroxide electrochemistry on platinum: towards understanding the oxygen reduction reaction mechanism, *Phys. Chem. Chem. Phys.* 14 (2012) 7384–7391.
- [25] Z. Lu, G. Chen, S. Siahrostami, Z. Chen, K. Liu, J. Xie, L. Liao, T. Wu, D. Lin, Y. Liu, T.F. Jaramillo, J.K. Nørskov, Y. Cui, High-efficiency oxygen reduction to hydrogen peroxide catalysed by oxidized carbon materials, *Nat. Catal.* 1 (2018) 156–162.
- [26] I. Sirés, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow. A review, *Environ. Sci. Pollut. Res.* 21 (2014) 8336–8367.
- [27] M.A. Oturan, An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants: Application to herbicide 2,4-D, *J. Appl. Electrochem.* 30 (2000) 475–482.
- [28] P. Cañizares, C. Sáez, A. Sánchez-Carretero, M.A. Rodrigo, Synthesis of novel oxidants by electrochemical technology, *J. Appl. Electrochem.* 39 (2009) 2143–2149.
- [29] A. Galia, S. Lanzalaco, M.A. Sabatino, C. Dispenza, O. Scialdone, I. Sirés, Crosslinking of poly(vinylpyrrolidone) activated by electrogenerated hydroxyl radicals: A first step towards a simple and cheap synthetic route of nanogel vectors, *Electrochem. Commun.* 62 (2016) 64–68.
- [30] S. Lanzalaco, I. Sirés, M.A. Sabatino, C. Dispenza, O. Scialdone, A. Galia, Synthesis of

- polymer nanogels by electro-Fenton process: investigation of the effect of main operation parameters, *Electrochim. Acta* 246 (2017) 812–822.
- [31] T. Holmes, T.J.G. Skalski, M. Adamski, S. Holdcroft, Stability of hydrocarbon fuel cell membranes: reaction of hydroxyl radicals with sulfonated phenylated polyphenylenes, *Chem. Mater.* 31 (2019) 1441–1449.
- [32] A.M. Dreizler, E. Roduner, Reaction kinetics of hydroxyl radicals with model compounds of fuel cell polymer membranes, *Fuel Cells*. 12 (2012) 132–140.
- [33] A. Medel, J.A. Ramírez, J. Cárdenas, I. Sirés, Y. Meas, Evaluating the electrochemical and photoelectrochemical production of hydroxyl radical during electrocoagulation proces, *Sep. Purif. Technol.* 208 (2019) 59–67.
- [34] K. Imamura, Y. Tada, H. Tanaka, T. Sakiyama, K. Nakanishi, Removal of proteinaceous soils using hydroxyl radicals generated by the electrolysis of hydrogen peroxide, *J. Colloid Interface Sci.* 250 (2002) 409–414.
- [35] J.P. Choi, A.J. Bard, Electrogenated chemiluminescence (ECL) 79. Reductive-oxidation ECL of tris(2,2'-bipyridine)ruthenium(II) using hydrogen peroxide as a coreactant in pH 7.5 phosphate buffer solution, *Anal. Chim. Acta.* 541 (2005) 141–148.
- [36] B.-T. Zhang, L.-X. Zhao, J.-M. Lin, Study on superoxide and hydroxyl radicals generated in indirect electrochemical oxidation by chemiluminescence and UV-Visible spectra, *J. Environ. Sci.* 20 (2008) 1006–1011.
- [37] J. Muff, L.R. Bennedsen, E.G. Søgaaard, Study of electrochemical bleaching of *p*-nitrosodimethylaniline and its role as hydroxyl radical probe compound, *J. Appl. Electrochem.* 41 (2011) 599–607.
- [38] A.J. Bard, Inner-sphere heterogeneous electrode reactions. Electrocatalysis and photocatalysis the challenge, *J. Am. Chem. Soc.* 132 (2010) 7559–7567.
- [39] H.S. Klapper, J. Goellner, Electrochemical noise from oxygen reduction on stainless

552 steel surfaces, *Corr. Sci.* 51 (2009) 144–150.

553 [40] N. Le Bozec, C. Comp, M.L.Ö. Her, A. Laouenan, Influence of stainless steel surface
554 treatment on the oxygen reduction reaction in seawater, *Corr. Sci.* 43 (2001) 765–786.

555 [41] J.M. Fang, R.C. Sun, D. Salisbury, P. Fowler, J. Tomkinson, Comparative study of
556 hemicelluloses from rice straw by alkali and hydrogen peroxide treatments, *Polym.*
557 *Degrad. Stab.* 66 (1999) 423–432.

558 [42] Y. Xiu-Juan, W. Hui, S. De-Zhi, S. Lai-Wen, W. Lan, Mechanism study of
559 electrochemical oxidation in the terylene diaphragm cell, *J. Environ. Sci.* 18 (2006) 33–
560 39.

561 [43] S. Strbac, The effect of pH on oxygen and hydrogen peroxide reduction on
562 polycrystalline Pt electrode, *Electrochim. Acta* 56 (2011) 1597–1604.

563 [44] C.-T. Wang, W.-L. Chou, Y.-M. Kuo, F.-L. Chang, Paired removal of color and COD
564 from textile dyeing wastewater by simultaneous anodic and indirect cathodic oxidation,
565 *J. Hazard. Mater.* 169 (2009) 16–22.

566 [45] M.M. Saleh, M.I. Awad, T. Okajima, K. Suga, T. Ohsaka, Characterization of oxidized
567 reticulated vitreous carbon electrode for oxygen reduction reaction in acid solutions,
568 *Electrochim. Acta.* 52 (2007) 3095–3104.

569 [46] G.R. Agladze, G.S. Tsursumia, B.I. Jung, J.S. Kim, G. Gorelishvili, Comparative study
570 of hydrogen peroxide electro-generation on gas-diffusion electrodes in undivided and
571 membrane cells, *J. Appl. Electrochem.* 37 (2007) 375–383.

572 [47] J.-M. Noël, A. Latus, C. Lagrost, E. Volanschi, P. Hapiot, Evidence for OH radical
573 production during electrocatalysis of oxygen reduction on Pt surfaces: consequences and
574 application, *J. Am. Chem. Soc.* 134 (2012) 2835–2841.

575 [48] B. Marselli, J. Garcia-Gomez, P.-A. Michaud, M.A. Rodrigo, C. Comninellis,
576 Electrogenation of hydroxyl radicals on boron-doped diamond electrodes, *J.*

Electrochem. Soc. 150 (2003) 79–83.

[49] A. Medel, E. Bustos, L.M. Apátiga, Y. Meas, Surface activation of C-sp³ in boron-doped diamond electrode, *Electrocatalysis* 4 (2013) 189–195.

[50] A. Medel, D. Patiño, E. Méndez, Y. Meas, L. Godínez, J. Manríquez, F. Rodríguez, A. Rodríguez, E. Bustos, Novel electrokinetic remediation system - boron doped diamond (EKR-BDD) process for the destruction of polyaromatic hydrocarbons (PAHs) in liquid phase, *Environ. Eng. Manage. J.* 14 (2015) 879–886.

[51] G.M. Eisenberg, Colorimetric determination of hydrogen peroxide, *Ind. Eng. Chem. - Anal. Ed.* 15 (1943) 327–328.

[52] A. Medel, E. Bustos, K. Esquivel, L.A. Godínez, Y. Meas, Electrochemical incineration of phenolic compounds from the hydrocarbon industry using boron-doped diamond electrodes, *Int. J. Photoenergy* 2012 (2012) 1–6.

[53] J. Kochany, E. Lipczynska-Kochany, Application of the EPR spin-trapping technique for the investigation of the reactions of carbonate, bicarbonate, and phosphate anions with hydroxyl radicals generated by the photolysis of H₂O₂, *Chemosphere* 25 (1992) 1769–1782.

[54] D. Wu, M. Liu, D. Dong, X. Zhou, Effects of some factors during electrochemical degradation of phenol by hydroxyl radicals, *Microchem. J.* 85 (2007) 250–256.

[55] A. Medel, E. Méndez, J.L. Hernández-López, J.A. Ramírez, J. Cárdenas, R.F. Frausto, L.A. Godínez, E. Bustos, Y. Meas, Novel electrochemical treatment of spent caustic from the hydrocarbon industry using Ti/BDD, *Int. J. Photoenergy* 2015 (2015) 1–18.

[56] J. Iniesta, P.A. Michaud, M. Panizza, C. Comninellis, Electrochemical oxidation of phenol at boron-doped diamond electrode. Application to electro-organic synthesis and wastewater treatment, *Electrochem. Commun.* 3 (2001) 346–351.

[57] X. Li, Y. Cui, Y. Feng, Z. Xie, J. Gu, Reaction pathways and mechanisms of the

electrochemical degradation of phenol on different electrodes, *Water Res.* 39 (2005) 1972–1981.

[58] M. Pimentel, N. Oturan, M. Dezotti, M.A. Oturan, Phenol degradation by advanced electrochemical oxidation process electro-Fenton using a carbon felt cathode, *Appl. Catal. B: Environ.* 83 (2008) 140–149.

[59] H. Czili, A. Horváth, Applicability of coumarin for detecting and measuring hydroxyl radicals generated by photoexcitation of TiO₂ nanoparticles, *Appl. Catal. B: Environ.* 81 (2008) 295–302.

[60] D. Bejan, E. Guinea, N.J. Bunce, On the nature of the hydroxyl radicals produced at boron-doped diamond and Ebonex[®] anodes, *Electrochim. Acta* 69 (2012) 275–281.

[61] Y. Nosaka, K. Ohtaka, N. Ohguri, A.Y. Nosaka, Detection of OH radicals generated in polymer electrolyte membranes of fuel cells, *J. Electrochem. Soc.* 158 (2011) 430–433.

[62] B. De Witte, J. Dewulf, K. Demeestere, H. Van Langenhove, Ozonation and advanced oxidation by the peroxone process of ciprofloxacin in water, *J. Hazard. Mater.* 161 (2009) 701–708.

[63] M.E. Simonsen, J. Muff, L.R. Bennedsen, K.P. Kowalski, E.G. Søgaaard, Photocatalytic bleaching of *p*-nitrosodimethylaniline and a comparison to the performance of other AOP technologies, *J. Photochem. Photobiol. A: Chem.* 216 (2010) 244–249.

[64] L. Diez, M.H. Livertoux, A.A. Stark, M. Wellman-Rousseau, P. Leroy, High-performance liquid chromatographic assay of hydroxyl free radical using salicylic acid hydroxylation during in vitro experiments involving thiols, *J. Chromatogr. B: Biomed. Sci. Appl.* 763 (2001) 185–193.

[65] S. Lis, M. Kaczmarek, Chemiluminescent systems generating reactive oxygen species from the decomposition of hydrogen peroxide and their analytical applications, *Trends Anal. Chem.* 44 (2013) 1–11.

627 [66] T. Olmez-Hanci, I. Arslan-Alaton, Comparison of sulfate and hydroxyl radical based
628 advanced oxidation of phenol, Chem. Eng. J. 224 (2013) 10–16.

Figure captions

Fig. 1. Effect of the reaction medium (0.5 mol dm^{-3}) on the cyclic voltammogram recorded on a Ti/BDD electrode. Counter electrode: Pt mesh; potential range: from -2.0 to +3.0 V vs Hg/Hg₂SO₄; scan rate: 100 mV s^{-1} ; temperature: 298 K.

Fig. 2. Effect of phenol concentration, from 0 to 140 mg dm^{-3} , on the cyclic voltammogram obtained with a Ti/BDD electrode in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. Counter electrode: Ti; potential range: from 0 to +1.4 V vs Hg|Hg₂SO₄; scan rate: 100 mV s^{-1} ; temperature: 298 K.

Fig. 3. Effect of phenol concentration ($150, 350$ and 550 mg dm^{-3}) on the electrochemical response of a Ti/BDD electrode by cyclic voltammetry in $0.5 \text{ mol dm}^{-3} \text{ M H}_2\text{SO}_4$. Counter electrode: Ti; range of potential: from -1.9 to +2.8 V vs Hg|Hg₂SO₄; scan rate: 100 mV s^{-1} ; temperature: 298 K. A blank voltammogram without phenol is also shown. The inset is a magnification of voltammograms with phenol.

Fig. 4. Effect of cathode material on the UV/Vis spectra obtained before and after 30 min of electrolysis of 50 cm^3 of $0.320 \text{ mmol dm}^{-3}$ phenol in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ using an undivided cell with a Ti/BDD anode at $E_{\text{an}} = +2.3 \text{ V}$ vs Hg|Hg₂SO₄ and 298 K.

Fig. 5. UV spectroscopy analysis of $\bullet\text{OH}$ production using coumarin as spin trap. (a) With a Pt cathode in the absence of O₂ (only atmospheric), (b) comparison of spectra using Ti, SS-304, graphite and Pt cathodes in the absence of O₂ (only atmospheric), and (c) with a Pt cathode in an O₂-saturated solution. The blank spectrum corresponds to the initial solution. Conditions: divided cell with 10 cm^3 of $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ and 0.1 mmol dm^{-3} coumarin at pH 3, stirring at 300 rpm, $E_{\text{cath}} = -0.305 \text{ V}$ vs Ag|AgCl, electrolysis for 15 h, temperature of 298 K. In plot c, *tert*-butanol was at 0.05 mol dm^{-3} .

Fig. 6. RP-HPLC analysis with a photodiode array detector for the indirect determination of $\bullet\text{OH}$ produced upon the electrochemical reduction of O_2 at Pt and graphite cathodes. (a) Change of normalized salicylic acid concentration and (b) variation of the proportion of the concentration of hydroxylated by-products formed during the reaction of salicylic acid with $\bullet\text{OH}$. Conditions: divided cell with 10 cm^3 of $0.05\text{ mol dm}^{-3}\text{ Na}_2\text{SO}_4$ and 5 mmol dm^{-3} salicylic acid at pH 3, stirring at 300 rpm, $E_{\text{cath}} = -0.305\text{ V}$ vs Ag|AgCl, temperature of 298 K.

Fig. 7. EPR analysis of $\bullet\text{OH}$ production in a divided cell with 10 cm^3 of an O_2 -saturated $0.05\text{ mol dm}^{-3}\text{ Na}_2\text{SO}_4$ solution at pH 3 under stirring at 300 rpm using a Pt cathode at $E_{\text{cath}} = -0.305\text{ V}$ vs Ag|AgCl and 298 K. (1) Only supporting electrolyte. (2) Initial time, after addition of 10 mmol dm^{-3} DMPO. Samples collected during the electrolysis: after (3) 10 min and (4) 60 min, and (5) after 60 min in the presence of 0.05 mol dm^{-3} *tert*-butanol.

Fig. 8. EPR analysis of $\bullet\text{OH}$ production by conventional Fenton's reaction carried out in 10 cm^3 of a 10 mmol dm^{-3} DMPO solution with $10\text{ mmol dm}^{-3}\text{ H}_2\text{O}_2$ and $1\text{ mmol dm}^{-3}\text{ Fe}^{2+}$ as reagents, under stirring at 300 rpm and 298 K after 10 min of treatment.

Fig. 9. UV/Vis spectroscopy analysis of H_2O_2 generation from the electrochemical reduction of O_2 dissolved in 10 cm^3 of a $0.05\text{ mol dm}^{-3}\text{ Na}_2\text{SO}_4$ solution, in the absence and presence of 0.05 mol dm^{-3} *tert*-butanol, at pH 3.0 under stirring at 300 rpm in the cathodic compartment of a divided cell with a Pt cathode after 60 min of electrolysis at $E_{\text{cath}} = -0.305\text{ V}$ vs Ag|AgCl and 298 K.

Fig. 10. EPR analysis of $\bullet\text{OH}$ production by electrochemical reduction of H_2O_2 in 10 cm^3 of a solution containing 10 mmol dm^{-3} DMPO and $100\text{ mmol dm}^{-3}\text{ H}_2\text{O}_2$ in $0.05\text{ mol dm}^{-3}\text{ Na}_2\text{SO}_4$ at pH 3 and stirred at 300 rpm in the cathodic compartment of a divided cell with a Pt cathode, after (1) 10 min and (2) 60 min of electrolysis at $E_{\text{cath}} = -0.305\text{ V}$ vs Ag|AgCl. The solution was

previously deoxygenated by bubbling N₂ gas, and a N₂ atmosphere was kept over the solution during the electrolysis.

Fig. 11. EPR analysis of •OH production by electrochemical reduction of H₂O₂ under the same conditions of Fig. 10 after 10 min of electrolysis, but using a (1) SS-304, (2) graphite and (3) Ti cathode.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Table 1

List of reactions of interest in this work.

Reaction	Number	Reaction	Number
$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	(1)	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	(19)
$\text{H}_2\text{O} \rightarrow \bullet\text{OH} + \text{H}^+ + \text{e}^-$	(2)	$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	(20)
$2\bullet\text{OH} \rightarrow \text{H}_2\text{O}_2$	(3)	$\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	(21)
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	(4)	$\bullet\text{OH} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}$	(22)
$2\text{H}_3\text{O}^+ + 2\text{e}^- \leftrightarrow \text{H}_2 + 2\text{H}_2\text{O}$	(5)	$\text{H}_2\text{O}_2 + \bullet\text{OH} \rightarrow \text{HO}_2\bullet + \text{H}_2\text{O}$	(23)
$\text{H}_2\text{O}_2 + \text{e}^- \rightarrow \bullet\text{OH} + \text{OH}^-$	(6)	$\text{O}_2 + 2\text{H}^+ + 3\text{e}^- \rightarrow \bullet\text{OH} + \text{OH}^-$	(24)
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	(7)	$\text{CO}_2 + \text{NaOH} \rightleftharpoons \text{NaHCO}_3$	(25)
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	(8)	$\text{NaHCO}_3 + \text{NaOH} \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$	(26)
$\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^{\bullet-}$	(9)	$\bullet\text{OH} + \text{CO}_3^{2-} \rightarrow \text{OH}^- + \text{CO}_3^{\bullet-}$	(27)
$\text{O}_2^{\bullet-} + 2\text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}_2$	(10)	$\bullet\text{OH} + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{\bullet-}$	(28)
$2\text{O}_2^{\bullet-} + 2\text{H}^+ \rightarrow {}^1\text{O}_2 + \text{H}_2\text{O}_2$	(11)	$\text{C}_9\text{H}_6\text{O}_2 + \bullet\text{OH} \rightarrow \text{C}_9\text{H}_6\text{O}_3 + \text{H}^+$	(29)
$\text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^-$	(12)	$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \bullet\text{OH} + \text{OH}^-$	(30)
$\text{H}_2\text{O}_2 \rightleftharpoons \text{H}^+ + \text{HO}_2^-$	(13)	$\text{Ti(IV)} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{TiO} + \text{H}_2\text{O}$	(31)
$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HO}_2^-$	(14)	$2\bullet\text{OH} \rightarrow \text{H}_2\text{O}_2$	(32)
$\text{H}_2\text{O}_2 + \text{HO}_2^- \rightarrow \bullet\text{OH} + \text{O}_2^{\bullet-} + \text{H}_2\text{O}$	(15)	$\text{H}_2\text{O}_2 + \bullet\text{OH} \rightarrow \text{HO}_2\bullet + \text{H}_2\text{O}$	(33)
$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^-$	(16)	$\text{HO}_2\bullet + \text{HO}_2\bullet \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	(34)
$2\text{HO}_2^- \rightarrow 2\text{OH}^- + \text{O}_2$	(17)	$\bullet\text{OH} + \text{HO}_2\bullet \rightarrow \text{O}_2 + \text{H}_2\text{O}$	(35)
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	(18)	$\text{H}_2\text{O}_2 + \text{H}^+ + \text{e}^- \leftrightarrow \bullet\text{OH} + \text{H}_2\text{O}$	(36)