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The Generation of Hydroxyl Radicals and Electro-oxidation of Diclofenac on Pt-doped SnO_2-Sb electrodes

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Abstract

Pt-doped SnO_2-Sb electrodes constitute promising candidates for the electrochemical abatement of refractory pollutants, but their efficacy to oxidize emerging pollutants remains uncertain. In this work, the electrochemical oxidation of diclofenac, pharmaceutical pollutant, on Pt-doped Ti/SnO_2-Sb electrodes has been studied by cyclic voltammetry and galvanostatic treatment in neutral medium. In parallel, the capability of these anodes to generate hydroxyl radicals ($^{\bullet}$OHs) has been analysed by in-situ UV spectroelectrochemical measurements. For comparison purposes, the responses of Ti/SnO_2-Sb and commercial Ti/Pt and BDD anodes were also evaluated. The voltammetric and electrolysis results show that the different Ti/SnO_2-Sb anodes can effectively oxidize and mineralize diclofenac, so their electrochemical activity lies in between that of Ti/Pt and BDD. The incorporation of small amounts of Pt (3-13 at.%) into the SnO_2-Sb coatings, despite hindering the $^{\bullet}$OHs generation, enhances the kinetics and efficiency for diclofenac oxidation and mineralization. This better overall response is attributed to a synergy between diclofenac-Pt interaction and efficient $^{\bullet}$OHs generation. Pt-doped Ti/SnO_2-Sb electrodes are then presented as a cheaper potential alternative to BDD for treating pharmaceutics pollutants in waters.

Keywords: electrocatalysis; anodic oxidation; Tin dioxide electrodes; hydroxyl radicals; diclofenac removal

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1. Introduction

Diclofenac, a nonsteroidal anti-inflammatory, analgesic, and antipyretic drug, is one of the most widely available pharmaceuticals worldwide [1]. Considering the continued release, biodegradation resistance and persistence [2-7], and/or toxic effects [8-11] of diclofenac, it is necessary to develop new methodologies for its elimination.

Various technologies have been proposed and reviewed for the removal of diclofenac [2,12-16]. Based on the generation of physisorbed hydroxyl radicals ($^{\bullet}$OHs), the anodic oxidation of pollutants constitutes probably the simplest advanced oxidation process (AOP) [17-20] and, thus, one of the most promising methods for the degradation of this drug [21]. This technology gathers several advantages to remove toxic biorefractory organic compounds [22]. However, its feasible application relies on the nature of the anode, which determines the efficiency and selectivity of the oxidation process, and the cost and durability [17-20,23].

To now, there are few studies on the anodic oxidation of diclofenac and most of them have been carried out with the Boron-Doped Diamond (BDD) anode [24-27], demonstrating its capability to full mineralization and toxicity reduction. Despite its good performance, the practical utilization of the BDD is limited by its high cost and fragility (because it is generally supported as a thin film on silicon wafers). On the other hand, other electrodes, like Pt [25,28], PbO_2 [27] and carbon materials [24,28], were also investigated for diclofenac oxidation.

Exhibiting a high overpotential for the oxygen evolution reaction (OER), non-active SnO_2-Sb anodes constitute a promising cheaper and efficient alternative for the electro-oxidation of pollutants [17,29,30]. It was found that the incorporation of a small percentage of Pt (3-13 metal atomic percent (at.%)) remarkably increases their short service life [31,32] and their catalytic activity for phenol degradation [33,34] in different electrolytes. Hence, both fundamental and practical studies on the electrocatalytic properties and potential applicability of these anodes have aroused great interest.

It is generally assumed that the performance of a given anode towards the electrochemical abatement of organic pollutants is correlated with its capability to generate oxidizing $^{\bullet}$OHs. Then, considering the observed catalytic effects of Pt [33,34], a promotion of $^{\bullet}$OHs generation would be expected by incorporating Pt into the SnO_2-Sb anodes. Nevertheless, in a recent study [35] the electrocatalytic effect of Pt has been associated to a strong specific adsorption of phenol on Pt/PtOx sites. Despite this controversy, the influence of Pt doping on the capability of SnO_2-Sb anodes to produce $^{\bullet}$OHs has been never investigated. Moreover, the catalytic activity of Pt-doped or undoped SnO_2-Sb anodes for the electro-oxidation of diclofenac has been never explored.

This work presents a study on the electrocatalytic activity of various Ti/SnO_2-Sb anodes towards the generation of $^{\bullet}$OHs and the oxidation and mineralization of diclofenac, as one of the most important pharmaceuticals, in neutral medium. The effect of the Pt content on the SnO_2-Sb coating is investigated. For comparison purposes, the performance of Ti/Pt and BDD commercial anodes has been also analyzed. Considering that the anodic removal of diclofenac is a complex reaction, involving various concurrent electrochemical processes, the catalytic activity of the different anodes was studied by different techniques, such as cyclic voltammetry (CV), in-situ UV spectroelectrochemical measurements and galvanostatic electrolysis, and by using different fixed electrochemical conditions.

These conditions were selected with the intention of better discerning the electrocatalytic response of the electrodes, without optimization of the experimental conditions.

2. Experimental

In the course of diclofenac removal by anodic treatment, three main electrochemical processes may occur simultaneously on the electrode surface: (i) the direct oxidation without mediation of $^{\bullet}$OHs; (ii) the mediated oxidation involving the generation of $^{\bullet}$OHs; and (iii) the OER. Thus, in order to provide a comprehensive picture of the electrocatalytic activity of the electrodes, these coupled processes

were studied concurrently and separately. The first two reactions have been individually studied by CV and in-situ UV spectroelectrochemical measurements, respectively. Studies on the OER were previously reported [31,32,36]. The complex reaction, diclofenac removal, was investigated by galvanostatic electrolysis. It is noteworthy to remark, then, that the electrochemical conditions used to better decouple the processes in CV and in-situ UV techniques were different and, therefore, did not try to be representative of those of the galvanostatic removal of diclofenac.

2.1. Electrode materials

Antimony and/or platinum doped tin oxide electrodes were prepared in our lab by conventional thermal decomposition of the salt precursors ($SnCl_4x5H_2O$ (Aldrich), $SbCl_3$ (Fluka) and H_2PtCl_6 (Aldrich) in acidified absolute ethanol (J.T. Baker) onto Ti substrate in the form of mesh or plate (INAGASA S.A.). The composition and nomenclature of the studied electrodes was Ti/SnO_2-Sb-Pt(x%), with Sb = 13 at% and x = 3 and 13 at% Pt (metal atomic composition); the Ti/SnO_2-Sb electrode without Pt has been also studied. Details on the preparation and physico-chemical properties of this type of electrodes can be found in the literature [31,34-38]. The Ti/Pt mesh (INAGASA S.A.) and BDD (Si/BDD, Adamant Technologies) plate electrodes were commercially supplied. Prior the electrochemical measurements, all the electrodes (plates or meshes) were submitted to a galvanostatic pre-treatment at 10 mA/cm^2 for 5 min to clean and stabilize the surface.

2.2. Electrochemical behavior towards diclofenac oxidation. Cyclic voltammetry

The electrocatalytic response of the different electrodes towards diclofenac oxidation was studied by cyclic voltammetry. Moreover, a polycrystalline Pt electrode with well-known electrochemical features, was used as model electrocatalyst to study the interaction of Pt with diclofenac. Prior usage, the surface of this electrode was thermally cleaned and subsequently protected from the laboratory atmosphere by a droplet of ultrapure water of 18.2 MΩ cm obtained from a Milli-Q® Advantage A10 water purification system (Merck Millipore).

The voltammetric measurements were performed in a conventional glass-made three-electrode cell by using a VSP Biologic potentiostat (Bio-logic Science Instruments). 0.5 M Na_2SO_4 (Merck p.a.) solutions, without or with 200 ppm sodium diclofenac (Sigma-Aldrich, molecular weight 318.1 g/mol), were prepared with ultrapure water and used as electrolyte. Since dissolved O_2 can affect the voltammetric response of the anodes, especially when containing Pt species, the solutions were degassed by N_2 bubbling for 20 min prior characterization. A Pt wire and an $Ag/Ag/Cl^-$(3 M KCl) electrode immersed in the same solution were used as counter and reference electrodes, respectively. A constant scan rate of 50 mV s^{-1} was used to record the cyclic voltammograms and the current densities were calculated by using the geometric area of the electrodes immersed in the electrolyte (2 cm^2 for all the electrodes, instead of 1 cm^2 for the BDD anode.

The voltammetric charge associated to diclofenac oxidation prior the OER (Q_{oxid}/Q_{blank}) was used in this work to quantitatively estimate the capability/affinity of the different anodes for the direct (non-$^{\bullet}$OH-mediated) oxidation of diclofenac [33,39]. This charge was calculated by integrating the positive current in the potential range where the signal in the presence of diclofenac overpasses that of the blank experiment without diclofenac (Q_{oxid}), and normalizing by the charge of the blank experiment (Q_{blank}), within the same potential range, to correct the contribution of a variant electrical double-layer (see details in the Figure S1 of the supporting information, SI).

2.3. Electrolysis runs

The capability of the different electrodes to electrochemically abate diclofenac was explored by using galvanostatic experiments in an undivided filter-press cell, with a plane electrode area of 20 cm^2, operated in batch recirculation. A volume of 200 cm^3 of 200 ppm diclofenac + 0.5 M Na_2SO_4 aqueous solution was continuously pumped through the cell and a jacketed reservoir for temperature control at 298 K during the experiment. The aqueous solutions were made up with distilled water. The different electrodes in the form of expanded meshes and the BDD plate were used as anodes and

a stainless steel (310L) plate acted as cathode in all the experiments. A constant current of 1 A (current density = 50 mA cm^{-2}) was applied for 5 h of electrolytic treatment and different aliquots were taken as a function of time to follow the extent diclofenac degradation. This current density value was arbitrarily chosen to get a meaningful comparative response of the electrodes within the 5h-experiments.

The concentration and transformation of diclofenac was monitored by UV-vis absorption spectroscopy (Jasco V-670 UV-vis-NIR spectrometer) over the wavelength range of 200-400 nm (see the calibration data in the Figure S2 of the SI) and the total organic carbon (TOC) was measured in a TOC Analyser (Shimadzu). Moreover, the electrode potential of the anodes was followed by using an Ag/AgCl/3M KCl reference electrode externally connected with a luggin capillary. Respect to the electrolyte, no significant changes on the solution pH were identified during the electrolytic experiments (see section 3.3.), so pH monitoring or the use of a buffer were considered unnecessary.

The efficiency of the anodes for diclofenac oxidation (Eff_{Diclof}, in %) and TOC removal (Eff_{TOC}, in %) have been calculated according to the following equations:

$$Eff_{Diclof} = \frac{[Diclof]_f - [Diclof]_0}{[Diclof]_0} x\ 100 \quad (1)$$

$$Eff_{TOC} = \frac{[TOC]_f - [TOC]_0}{[TOC]_0} x\ 100 \quad (2)$$

where *f* and *0* refer to the final and initial concentrations, respectively, of diclofenac and TOC. The mineralization current efficiency (MCE, in %) at a given time (*t*, in s) was calculated by using the following equation:

$$MCE = \frac{n\ F\ V\ \Delta(TOC)}{m\ I\ t} x100 \quad (3)$$

where *F* is the Faraday constant (96485 C mol^{-1}), *V* is the solution volume (L), *Δ(TOC)* is the TOC decay at a given time ($[TOC]_t - [TOC]_0$, in g L^{-1}), *m* is the number of carbon atoms per molecule of diclofenac (14 C atoms), *I* is the applied current (A), and *n* is the number of electrons consumed for the mineralization of one molecule of diclofenac assuming the following reaction [25]:

$$C_{14}H_{10}Cl_2NO_2^- + 26\,H_2O \rightarrow 14\,CO_2 + 2\,Cl^- + NH_4^+ + 58\,H^+ + 58\,e^- \quad (4)$$

2.4. Generation of hydroxyl radicals

The determination of the $^{\bullet}$OHs was carried out spectrophotometrically by means of the reaction with N,N-dimethyl-p-nitrosoaniline (RNO), used as radical scavenger, at constant potential [40,41]. The method is based on the direct relationship between the generation of the $^{\bullet}$OH radicals and the depletion of the RNO concentration (RNO bleaching), which can be followed by UV spectroscopy. To do that, a conventional UV cell was adapted to become a three-electrodes electrochemical cell for in-situ UV electrochemical degradation of RNO (Figure 1a). The counter electrode (CE) was a Pt wire and a wire of Ag acted as pseudo-reference electrode (RE), whereas the studied anodes were used as working electrode (WE) with a exposed geometric area of 2 cm^2, instead for the BDD, working with 1 cm^2. A calibration curve was made before the experimental series by following the dependence of the absorbance band at λ = 440 nm of RNO with its concentration in a range of 2-50 µM (see Figure S3 in the SI).

Figure 1b depicts the experimental set-up used for the electrochemical measurements. Each WE was allocated into the electrochemical cell containing a 20 µM RNO aqueous solution, and checking that the submerged electrodes do not block the pathway of the light beam. Then the cell was placed inside a UV-Vis-NIR JASCO V-670 spectrophotometer and connected to an Origalys OrigaFlex500 Potentiostat-galvanostat. The external connecting wires were passed through the equipment dark chamber door without letting the external light to enter.

Before starting the electrochemical experiments, a UV spectrum was measured between 600 and 200 nm (labelled as 0 min) to check the initial conditions of the RNO solution, ruling out any potential degradation of this compound during the time stored. In this sense, if the starting band absorbance of the used RNO solution deployed more than 3% from the controlled expected one, a new solution was prepared to start the experiment.

Once checked, a chronoamperometric method was programmed to the potentiostat by the Origamaster software. A constant potential of 1.7 V (vs. Ag/AgCl/3M KCl) was settled to be applied for 2 hours, taking a UV spectrum every 2 minutes during the first 10 minutes, and thereafter every 10 minutes. This potential was selected because it is above (but not far from) the onset of the OER on the different Ti/SnO_2-Sb (without and with Pt) and Ti/Pt anodes (see below Figure 2). Larger potentials could be detrimental for this experiment because of the promotion of the OER [42] and/or direct and over-oxidation of RNO. In the case of BDD, a higher constant potential of 2.4 V (vs. Ag/AgCl/3M KCl) was also tested. The resulting spectra were recorded in the PC by the Spectra ManagerTM software. All the solutions used for calibration and electro-oxidation of RNO were prepared with ultrapure water. Moreover, additional experiments were performed also at constant current (from 5 to 50 mA/cm^2) to confirm the trends found potentiostatically. Nevertheless, these experiments were necessarily performed ex-situ because of the constraints caused by strong bubbling in the in-situ set up.

3. Results and Discussion

3.1. Cyclic Voltammetry

The electrochemical behavior of diclofenac on the different electrodes was studied by cyclic voltammetry. This analysis mainly encompassed the relatively low potentials prior (and therefore excluding) the OER, thus, it enabled to decouple and study diclofenac interaction and oxidation on the anode surface in the absence of $^{\bullet}OH$s.

Figure 2 compares the voltammetric responses of the studied electrodes in the absence and presence of diclofenac. Respect to commercial anodes, the negligible oxidation currents observed for Ti/Pt in the presence of diclofenac (Figure 2a), resulting in a normalized oxidation charge (Q_{oxid}/Q_{blank}) close to 1 (Table 1), was indicative of a poor catalytic response. However, two clear oxidation processes were discerned for BDD (Figure 2b). In agreement with literature, the first process at ca. 0.95 V may

be associated to the direct electro-oxidation of diclofenac on the surface of BDD [23,43-46]; while the sharp current rise from 1.50 V, towards the potential range where the OER takes place (see the voltammogram of BDD anode in the blank electrolyte), might involve the $^{\bullet}$OHs-mediated oxidation of diclofenac. The calculated Q_{oxid}/Q_{blank} for these processes was remarkably high, ca. 21, entailing a superb activity for diclofenac oxidation.

For the Ti/SnO_2-Sb electrode without Pt (Figure 2c), an anodic current rise is observed above 0.5 V in the presence of diclofenac. Because it starts at ca. 1 V below the onset of the OER, this process may be attributed to the direct (non-$^{\bullet}$OH mediated) electro-oxidation of adsorbed and/or solution diclofenac. Such a direct oxidation has been also observed on other metal oxide anodes [47-49]. Moreover, the diclofenac oxidation current increased with the augment of Pt content in the Pt-doped Ti/SnO_2-Sb electrodes (Figures 2d and 2e). Thus, the normalized oxidation charge (Q_{oxid}/Q_{blank}) for the electrode without Pt (1.45) increased up to ca. 1.7 and 1.8 for the electrodes with 3 and 13 at.% Pt, respectively (Table 1).

Given the remarkable activity observed by polycrystalline Pt (see Figure S4 in the SI), the obtained results are attributed to a significant interaction and oxidation activity of diclofenac on the Pt present in the Ti/SnO_2-Sb electrodes. Discrepancies with the case of Ti/Pt may be explained by the different properties of Pt in these electrodes, prepared by completely distinct methods, which greatly affect the electrocatalytic activity of Pt catalysts [50] (see further discussion in the SI).

3.2. Generation of hydroxyl radicals

The capability of the different electrodes to generate hydroxyl radicals was related to the kinetics of RNO bleaching followed by in-situ electrochemical UV spectroscopy. The evolution of current density during the potentiostatic experiments can be found in the SI (Figure S5). The absorbance at the wavelength of the maximum, i.e. the concentration of RNO, started to decrease after applying the constant potential of 1.7 V on all the different tested anodes (see as example the spectra of the

different Ti/SnO_2-Sb anodes in Figures 3a-c, and those of the other electrodes in Figure S6 of the SI), according of the following reaction:

$$RNO + {}^{\bullet}OH \rightarrow RNO({}^{\bullet}OH) \quad (5)$$

The concentration of RNO at a given time ([RNO]) was then calculated with the calibration curve. It was observed that, in all cases, the variation of RNO concentration followed an exponential-like decay, so it was fitted to a pseudo-first order kinetics according to the expression:

$$Ln\frac{[RNO]}{[RNO]_0} = -k_{app} \cdot t \quad (6)$$

where $[RNO]_0$ and $[RNO]$ are the initial and time-dependent concentrations of RNO, and k_{app} refers to the apparent first-order rate constant for RNO concentration decay ($k_{app} = [{}^{\bullet}OH] \cdot k$, assuming a constant "pseudo steady-state" concentration of ˙OHs during the measurements). Considering that (i) the reaction rate of RNO with ˙OHs is very fast (ca. 1.25 x 10^{10} M^{-1} s^{-1}); (ii) the bleaching of RNO is very selective to oxidation by ˙OHs; and (iii) the (direct) non-˙OH -mediated oxidation of RNO may be negligible, as reported in previous works (see the references [17,40-42]); hence, the rate constant for RNO concentration (k_{app}) decay may approximate that for ˙OHs generation ($k_{app(\cdot OH)}$).

The logarithm of the normalized RNO concentration was plotted versus the reaction time (Figure 3d). As observed in the figure, in all cases the experimental data followed a straight trend with R^2 > 0.99, validating the proposed kinetic model [41,42]. The apparent rate constants for ˙OHs generation on the different anodes were deduced from the slope of these kinetic plots and are collected in Table 1, and the current densities passing through the different anodes follow the same trend (Fig. S5). As it can be observed, at 1.7 V the fastest generation of ˙OHs was observed on the Ti/SnO_2-Sb and BDD anodes with apparent rate constants of 0.0130 and 0.132 min^{-1}, respectively. These results agree with literature, which generally attributes a higher capability to produce ˙OHs to non-active anodes [17-20,23]. Nevertheless, it is worthy to mention that the geometric are of the BDD was the half that of the Ti/SnO_2-Sb. Moreover, it can be inferred that 1.7 V, the potential used for comparison, is not a too high potential for BDD. Thus, a spectroelectrochemical test of BDD carried out at 2.4 V (vs.

Ag/AgCl/Cl^-(3M)) showed that the rate constant considerably increased to 0.0161 min^{-1} (Table 1). On the contrary, Ti/Pt exhibited the slowest rate for $^{\bullet}OH$ generation (Table 1) [51]. This result is in line with the comparatively poorer performance of this anode to electro-oxidize refractory organics [17,20].

The incorporation of Pt into the SnO_2-Sb anode decreases the rate constants for $^{\bullet}OH$ generation (Table 1). This is a new interesting result that cannot be expected from the literature, since Pt doping was found to thermodynamically and kinetically promote the OER [35,36], and the electrocatalytic activity towards organics oxidation [33-35]. Considering the mechanism proposed by Comninellis et al. [17], which regards the $^{\bullet}OHs$ as reaction intermediates for both the OER and organic oxidation, and the changes on k_{app} observed in this work, it is hypothesized that the presence of Pt may alter (weaken) the physisorption strength of $^{\bullet}OHs$ (reduce the potential needed) to form O_2 or react with organic molecules, but not the rate of $^{\bullet}OH$ formation (water discharge). In other words, the promotion and acceleration of OER and/or organic oxidation induced by Pt may come from destabilization of surface-$^{\bullet}OHs$, instead of a faster $^{\bullet}OHs$ generation. This agrees with the true electrocatalytic effects observed for Pt doping on the OER and phenol electro-oxidation [35].

The found trend in $^{\bullet}OHs$ generation rate over the different anodes was confirmed by carrying the experiments at different constant current densities, observing larger differences in reaction rates at higher current densities (figures not shown). Nevertheless, these experiments did not enable to calculate accurate rate constants because of a promoted OER [42].

3.3. Electrolysis performance

Finally, the response of the different electrodes to electro-oxidize diclofenac was also tested under galvanostatic conditions in a flow electrochemical filter-press cell. The diclofenac concentration was followed by UV spectroscopy. Figure 4 depicts the evolution of the diclofenac absorption band centered at 275 nm during the electrolytic experiments with the different electrodes.

In all cases, it is observed that the absorption band progressively decreases with time, without any shift of its position. Considering the strong effect of pH on the wavelength of the maximum absorption of diclofenac in UV spectra, this experimental fact may be indicative of non-significant changes on pH during electrolysis. Thus, while the anodic processes generate protons the cathodic ones produce base, so that the bulk pH remain neutral. Nevertheless, the oxidation of diclofenac might occur in an acid local environment, the local pH depending on the current density. Moreover, other bands are not formed during the course of the electrolysis, indicating that the generated by-products from diclofenac oxidation do not seem to interfere the UV analysis of diclofenac.

Figure 5a represents the calculated diclofenac concentration versus electrolysis time. The generally observed decay in diclofenac concentration pointed out that all the tested electrodes were effective to electro-oxidize diclofenac. Furthermore, the parallel decrease in TOC (Figure 5b), together with negligible variations in the total inorganic carbon, revealed that all the anodes can also mineralize this compound. The efficiencies for diclofenac oxidation and TOC removals were determined from the initial and final diclofenac and TOC concentrations, respectively, and are listed in Table 1. In addition, Table 1 also collects the calculated values for the mineralization current efficiency (MCE). These values did not exceed 10 % even for the most effective BDD anode. Nevertheless, it is important to remark that the optimization of neither the electrochemical variables nor current efficiencies was attempted in this work.

Respect to the concentration decays, they first followed a linear trend and became exponential after ca. 1 h of experiment. These regimes were initially envisioned by the kinetic model of Comninellis et al. [18,20,44,45] for the electrochemical combustion of organics on ideally non-active BDD, and observed also for the electro-oxidation of phenol on different metal oxides including Pt-doped SnO_2-Sb [34]. Details of the model applied for BDD and its derivation for non-ideal non-active electrodes can be found in these last references. Then, the concentration decays during the first hour of experiments were fitted to a pseudo zero-order kinetics:

$$[Diclof] = [Diclof]_0 - k_o t \quad (7)$$

and

$$TOC = TOC_0 - k_0' t \quad (8)$$

while the data within 1-5 h of experiments were fitted to a pseudo first-order kinetics:

$$[Diclof] = [Diclof]_0\, \beta \exp\left(-k_1 t + \frac{1-\beta}{\beta}\right) \quad (9)$$

and

$$TOC = TOC_0\, \beta \exp\left(-k_1' t + \frac{1-\beta}{\beta}\right) \quad (10)$$

where $[Diclof]_0$ and $[Diclof]$ are the initial and time-dependent concentrations of diclofenac; k_o and k_1 correspond to the zero-order and first-order rate constants for diclofenac oxidation; TOC and TOC_0 are the initial and time-dependent TOCs; k_0' and k_1' refer to the zero-order and first-order rate constants for TOC removal; and β is a dimensionless parameter depending on the applied and limiting current densities and the initial current efficiency, and reflects the condition at which the change from pseudo-zero to pseudo-first order regime occurs [34]. The plots of $[Diclof]$ or $\ln[Diclof]$ versus time were successfully fitted into straight lines with $R^2 > 0.99$ for all the studied anodes, thus, validating the application of the kinetic models. The rate constants were calculated from the slopes of these linear fittings and collected in Table 1.

Figure 5 shows that, as expected, BDD was the best anode to oxidize and mineralize diclofenac. This electrode reduced 100 % of diclofenac and 87 % of TOC in only 1 h, and enabled to reduce 100 % TOC in less than 3 h. These results agree with the extraordinary performance shown by this electrode to mineralize several organic pollutants [23-26,43-46]. Although it has been proved that it can directly oxidize diclofenac (section 3.1), the superior performance of BDD during electrolysis is mainly attributed to its facility to rapidly generate a large amount of highly oxidizing $^{\bullet}$OHs (section 3.2). In fact, the high potential of BDD during the electrolysis (+3.7 V vs. Ag/AgCl/Cl$^-$(3.5 M), average, see Table S1) may guarantee the generation of an enormous amount $^{\bullet}$OHs for such a fast

diclofenac electro-oxidation. Accordingly, the calculated rate constants for diclofenac oxidation and mineralization were remarkably higher compared to the other electrodes tested (Table 1). By contrast, Ti/Pt oxidized the 70 % of diclofenac and eliminated the 33 % of TOC in 5 h, presenting the slowest reaction kinetics (Table 1) and, overall, the worst performance among the studied anodes. This is in line with the poor activity of this anode for diclofenac oxidation observed by cyclic voltammetry and the slowest kinetics for producing $^{\bullet}$OHs (Table 1). It can be inferred, then, that this electrode working at +2.6 V vs. Ag/AgCl/Cl$^-$(3 M) (average) promoted the OER during the electrolytic experiment.

Regarding the SnO_2-Sb anodes, the performance of the SnO_2-Sb without Pt was found better than that of Ti/Pt. The faster reaction kinetics on this anode (Table 1) resulted in 83 % of diclofenac oxidation and ca. 40 % of TOC removal after 5 h treatment. This better response can be assigned to the faster formation of $^{\bullet}$OHs (Table 1) and/or their higher oxidizing power when they are produced on this non-active material (working at 2.65 V vs. Ag/AgCl/Cl$^-$(3 M)).

Figure 5 demonstrates that the introduction of Pt improves the electro-oxidative response of the Ti/SnO_2-Sb anode under galvanostatic conditions. Thus, with the introduction of 3 and 13 at.% Pt, the diclofenac oxidation efficiency increases up to 89 and 91 %, respectively, and that for TOC removal reaches relatively high values of ca. 53 and 61 %, respectively. Similar trends were found for the values of the mineralization current efficiencies for the different anodes (for example, see those calculated at 2 h provided in Table 1), remarking the intermediate performance of Ti/SnO_2-Sb-Pt anodes between those of expensive commercial anodes.

The effect of Pt on the electrocatalytic response of Ti/SnO_2-Sb anodes found for diclofenac oxidation has many similarities with that previously observed for phenol [33-35]. Independently of the electrolyte, in both cases Pt improves the direct (non-$^{\bullet}$OHs-mediated) oxidation of the pollutant prior OER and the pollutant removal by galvanostatic treatment, at least up to 3 % Pt. However, important differences can be found too, especially for galvanostatic treatments. First, in H_2SO_4 the electrode

with the highest amount of Pt (Ti/SnO_2-Sb-Pt (13%)) showed the lowest activity for phenol oxidation and mineralization [33], but it is the best one for the case of diclofenac in Na_2SO_4 (Fig. 5). Second, phenol and diclofenac in basic [34] and neutral medium (Fig. 5), respectively, have exhibited a change from pseudo-zero to pseudo-first order kinetics, while phenol in acid electrolyte showed a first-order regime during the whole electrolytic treatment, even for initial concentrations as high as 1000 ppm [33]. These varying results and effects may be explained by the relative contribution of the different processes involved, such as the pollutant-surface interaction/oxidation and the $^{\bullet}OH$ generation, at which the structure of the pollutant and the pH of the medium may play a relevant role. To explain the influence of Pt on the electro-oxidation of phenol in alkaline conditions, the specific adsorption of phenolate ions on Pt/PtO_x was proposed to facilitate their reaction with highly oxidizing $^{\bullet}OH$s formed on the SnO_2-Sb matrix [35]. However, the distinct rate for $^{\bullet}OH$s generation was not studied. Interestingly, the present work demonstrates that Pt incorporation slows down the rate for $^{\bullet}OH$s generation in neutral medium (Table 1). Then, the better response of these electrodes for diclofenac removal can be attributed to the promoted interaction of diclofenac with surface Pt species (observed by cyclic voltammetry, section 3.1), which could be even stronger than that with phenolate. In fact, previous studies on the electrochemical behavior of organic acids on Pt surfaces demonstrated a strong interaction and/or adsorption of these molecules through their carboxylic group [52,53]. Hence, it is hypothesized that the superior performance of Pt-doped SnO_2-Sb anodes towards diclofenac oxidation may be due to a strong interaction of diclofenac with Pt facilitated by the carboxylic group in this pollutant. Nevertheless, it is noteworthy to remark that all these hypotheses are based on the observation of voltammetric experiments and/or indirectly deduced from performance parameters, so that the use of additional or coupled powerful techniques are necessary to provide stronger evidences.

4. Conclusions

The voltammetric and galvanostatic study presented in this work demonstrates that Ti/SnO_2-Sb anodes, with or without Pt, can efficiently oxidize and mineralize diclofenac. The good performance of these electrodes has been voltammetrically observed at potentials below the OER, where they can directly oxidize diclofenac, as well as at high potentials during electrolysis experiments, where the oxidation is mainly mediated by hydroxyl radicals concurrently to the OER.

The calculated voltammetric oxidation charges, and the efficiencies and rate constants for diclofenac oxidation and TOC removal indicate that the incorporation of small amounts of Pt (3-13 at.%) remarkably enhances the performance of Ti/SnO_2-Sb anodes for diclofenac abatement (apart from other benefits, such as an enhanced service life [31,32]). Interestingly, this electrocatalytic effect on diclofenac removal is observed even though the Pt doping partly hinders the generation of $^{\bullet}$OHs, what supposes a completely new finding that contradicts what would be expected from the literature. From the observed strong interaction and good oxidation activity of diclofenac on polycrystalline Pt, the enhanced response of Pt-doped Ti/SnO_2-Sb anodes is assigned to an effective Pt-diclofenac interaction that may promote its oxidation directly and/or with the electrogenerated $^{\bullet}$OHs.

Comparisons with commercial anodes under similar experimental conditions show that the performance of the Ti/SnO_2-Sb anodes lies in between those of Ti/Pt and BBD. The obtained results, hence, enable to propose Pt-doped Ti/SnO_2-Sb anodes as potential cheaper alternatives to BDD for the elimination of pharmaceutics in wastewater.

Acknowledgements

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Supporting Information

Generation of Hydroxyl Radicals and Electro-oxidation of Diclofenac on Pt-doped SnO_2-Sb electrodes

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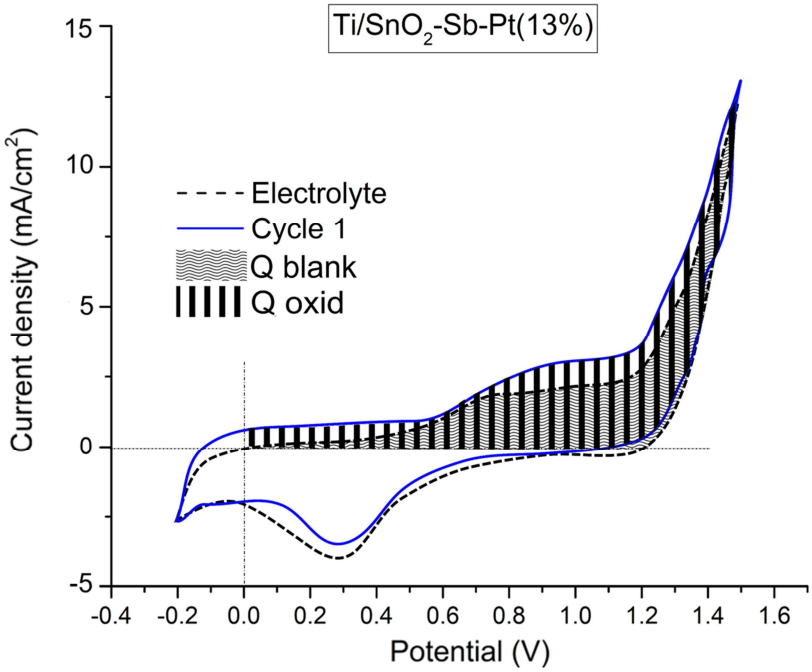

Figure S1. Voltammetric areas integreted for the calculation of the charge associated to diclofenac oxidation prior the OER (Q_{oxid}/Q_{blank}). Example for the Ti/SnO_2-Sb-Pt(13%) anode.

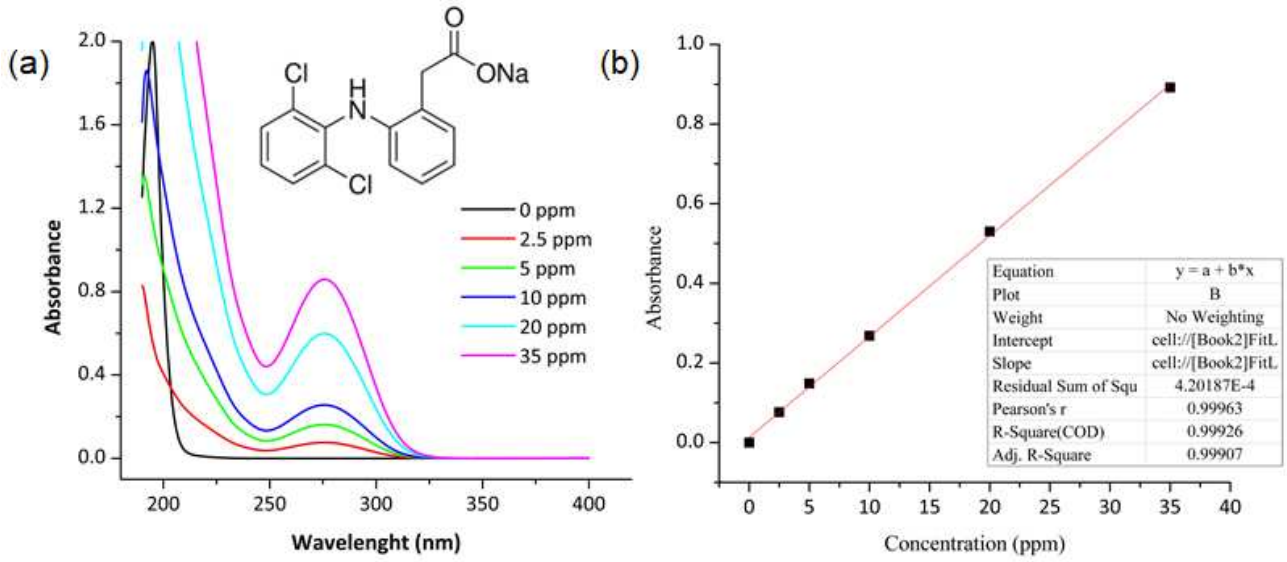

Figure S2. (a) UV spectra of 0.5 M Na_2SO_4 aqueous solutions with different sodium diclofenac concentrations; and (b) the calibration curve for spectroscopic determination of diclofenac.

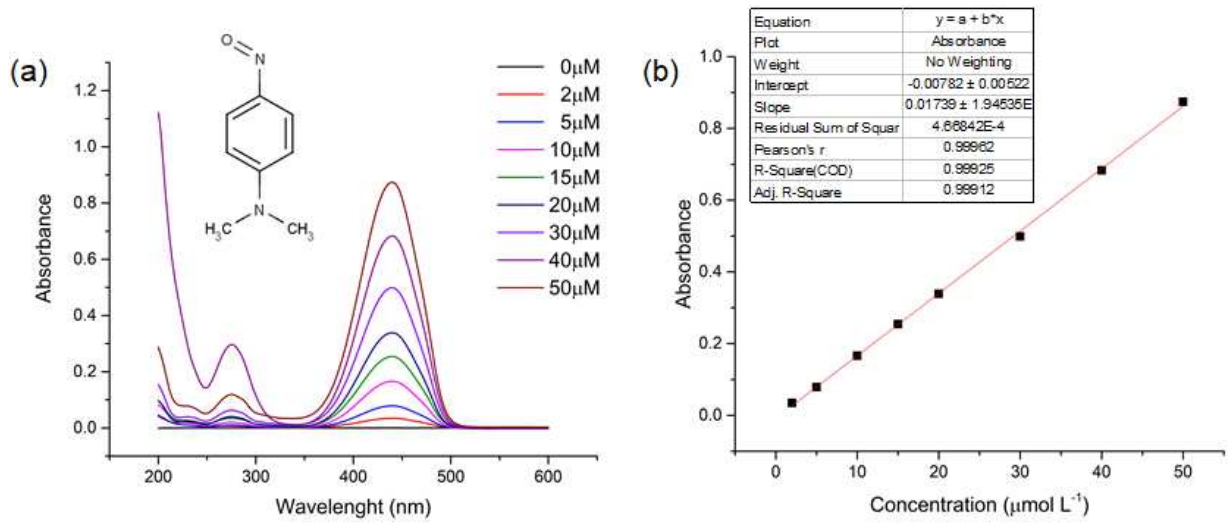

Figure S3. (a) UV spectra of differently concentrated RNO solutions; and the (b) calibration curve for spectroscopic determination of RNO.

Electrochemical behavior of diclofenac on polycristalline Pt studied by cyclic voltammetry

Figure S4 shows the response of a polycrystalline Pt electrode, used as model reference material, in the absence and presence of diclofenac. In the absence of diclofenac (black dash line), the voltammogram presents the characteristic hydrogen adsorption-desorption and reduction-oxidation peaks (H_a, H_d) as well as the Pt surface oxidation-reduction ($Pt_{ox}, PtOx_{red}$) processes [1].

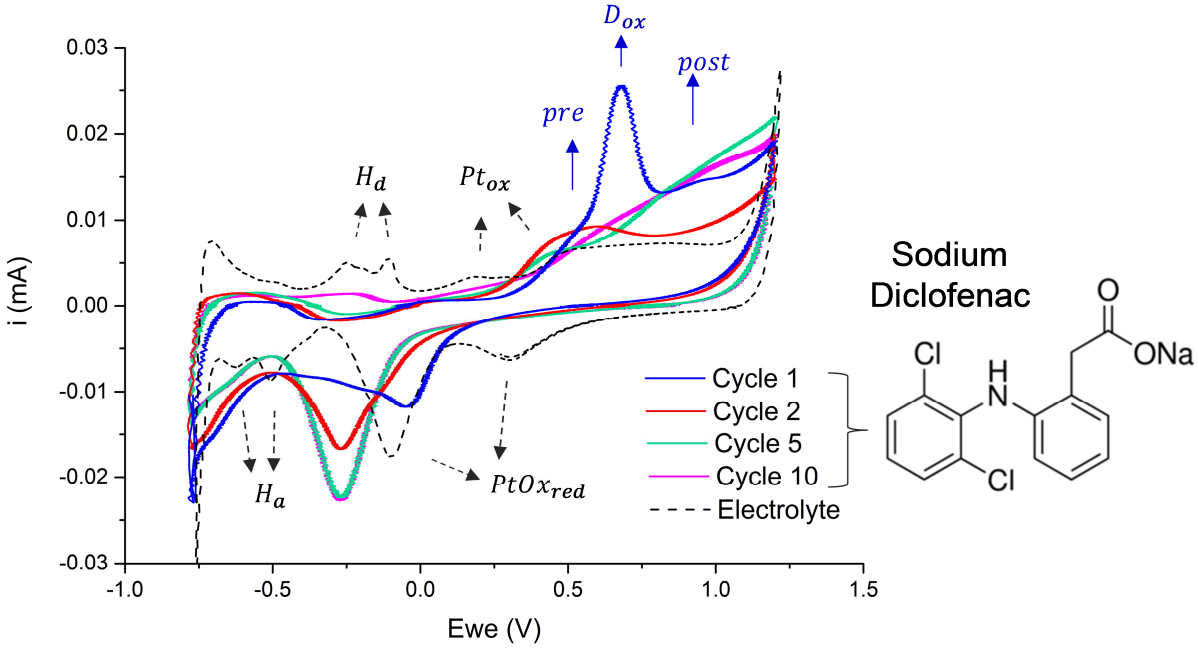

Figure S4. Successive cyclic voltammograms of a polycrystalline Pt electrode in 200 ppm diclofenac + 0.5 M Na_2SO_4 aqueous solution. Scan rate = 50 mV s^{-1}. Refence electrode Ag/AgCl/3M KCl.

In the presence of diclofenac (blue rigid line), however, the electrode shows a reduced current and no oxidation processes during the first forward cycle from -0.8 to 0.25 V. This suggests the adsorption of diclofenac on the Pt surface within this potential range. From 0.25 V, the anodic current rises and a defined oxidation peak (D_{ox}) centred at 0.68 V is clearly observed in the first cycle. Moreover, the overlapped processes before and after the peak (pre and $post$, respectively) are indicative of other concurrent oxidation processes. These processes are assigned to the non-$^{\bullet}$OH-mediated oxidation of adsorbed and/or solution diclofenac and derived oxidation by-products on Pt and/or PtOx surfaces.

During the reverse cathodic scan, the peaks attributed to reduction of surface PtOx species, centred at 0.32 V and -0.11 V, are remarkably affected, and only one cathodic peak of intermediate intensity and potential (at ca. -0.05 V) is observed. Similar effects were found with other organic compounds [2]. These effects may be assigned to changes in the pH (acidification), in the proximity of the electrode surface, during the positive scan as a consequence of the OER. This local acidity might also promote diclofenac protonation, affecting the chemistry of electroactive species. Nevertheless, this local acidification may be partly compensated by cathodic processes (hydrogen evolution reaction) during the reverse scan. On the one hand, these voltammetric changes could also indicate that the oxidation of surface Pt to PtOx during the forward cycle is influenced by concurrent diclofenac oxidation, and/or that the oxidation products cause an effect on the reduction process. In this sense, a progressive change on the electrochemical response of the Pt electrode was observed during the second and successive cycles (red and green rigid lines).

Particularly, the anodic peak at 0.68 V practically disappears in the 2nd cycle; the pre-oxidation process becomes important in the 2nd and subsequently vanishes upon cycling; and the relative intensity of the post-oxidation processes between 0.90 and 1.20 V increases. Moreover, the cathodic peak further shifts to -0.26 V and its intensity progressively increases with the number of cycles. All these observations reflected a significant interaction and effective oxidation of diclofenac and by-products on Pt, making it a promising dopant for diclofenac oxidation.

Differences in the electrocatalytic activity of the distinct Pt electrodes studied in this work

This work shows the electrochemical response of three different types of electrodes involving or containing Pt, namely Pt-doped Ti/SnO_2-Sb anodes (target) and polycrystalline Pt and Ti/Pt (for comparison purposes), and they exhibit quite different response towards diclofenac oxidation. This is quite normal and expected, since it is well known that the electrocatalytic activity of Pt catalysts is very sensitive to many factors, highlighting surface cleanliness, defects and arrangement of Pt atoms; Pt crystalline planes; dimensions and morphology of Pt phases; dispersion and surface area, etc. [3-5]. All these characteristics of Pt are mainly determined by the nature of the precursor and the preparation and pre-treatment methods.

Accordingly, these electrodes have no similarity in response because they have been prepared and pre-treated by different methods:

- As explained in the experimental section, for the polycrystalline Pt electrode "Prior usage, the surface of this electrode was thermally annealed and cleaned and subsequently protected from the laboratory atmosphere by a droplet of ultrapure water ..." This thermal treatment is achieved by a blue flame at very high temperatures, enabling to obtain a completely clean Pt surface with a characteristic surface atoms arrangement. Such a clean electrode presents a highly active and easily reproducible electrochemical response that makes it a model electrocatalyst for fundamental studies.

- On the contrary, the Ti/Pt electrode is a commercial product prepared by electrochemical deposition of a thin film of Pt onto a Ti substrate. This constitutes the feasible Pt electrode for practical application and cannot be thermally cleaned or annealed by using the previous method, since the high-temperature flame would make Pt to react with Ti support. Instead, this electrode is cleaned electrochemically (see details in the experimental section), so that its different cleaning degree and/or atomic surface arrangement may make this electrode considerably less active than polycrystalline Pt.

- Finally, the physico-chemical properties of Pt-doped Ti/SnO_2-Sb electrodes, prepared by thermal decomposition of proper metallic salt precursors, have been reported in previous papers [6-10]. Briefly, in these electrodes Pt/PtOx nano-/submicron domains are uniformly spread out over a matrix of SnO_2-Sb. Although both electrodes are cleaned by a similar electrochemical pre-treatment, the distinct structure of Pt phase in the form of small particles surrounded by such an effective matrix for $^{\bullet}OH$ generation may be responsible of the higher activity of Pt-doped Ti/SnO_2-Sb electrodes compared to Ti-supported bulk Pt films in Ti/Pt.

Table S1. Electrode potential of the different anodes and cell voltage reached during the 5h-galvanostatic oxidation of diclofenac at 50 mA cm^{-2}. Electrolyte (0.2 L) = 200 ppm diclofenac + 0.5 M Na_2SO_4.

Electrode	E_{ANODE} (V vs. Ag/AgCl/3M KCl)	Voltage (V)
Ti/Pt	2.57-2.68	4.9
BDD	3.89-3.77	6.0
Ti/SnO_2-Sb	2.08-2.65	6.0-6.5
Ti/SnO_2-Sb-Pt(3%)	1.83-1.90	4.4
Ti/SnO_2-Sb-Pt(13%)	2.12-2.08	4.8

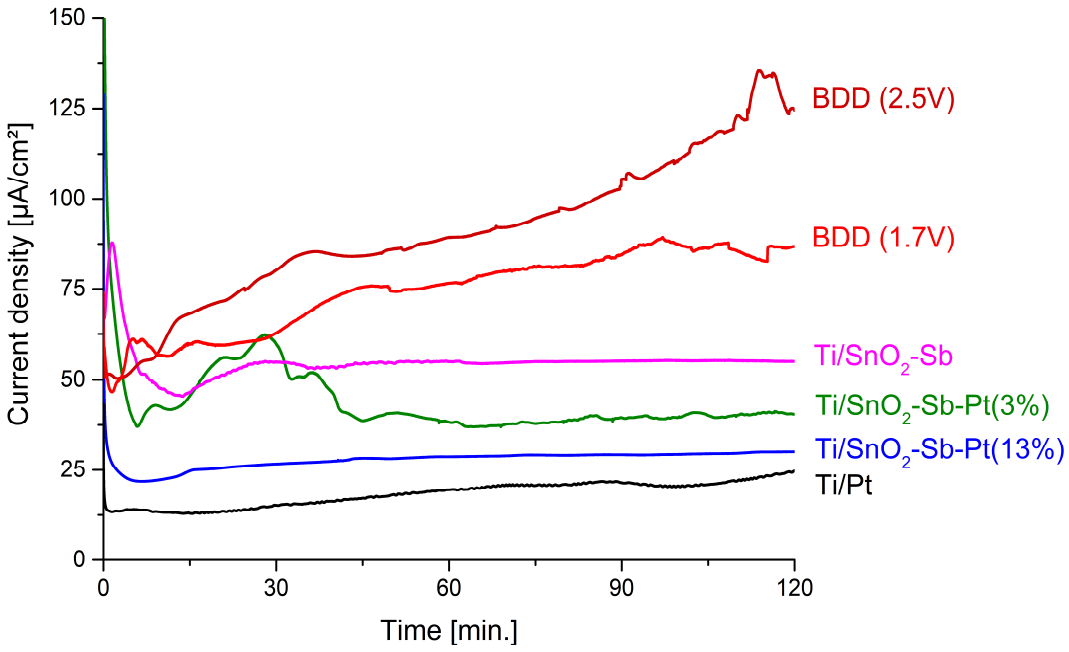

Figure S5. Evolution of current density during in-situ UV potentiostatic electrolysis of aqueous RNO solutions (2 x 10^{-5} mol dm^{-3}) with the different anodes at 1.7 V vs. Ag/AgCl/Cl^-(3 M) and BDD at 2.4 V vs. Ag/AgCl/Cl^-(3 M).

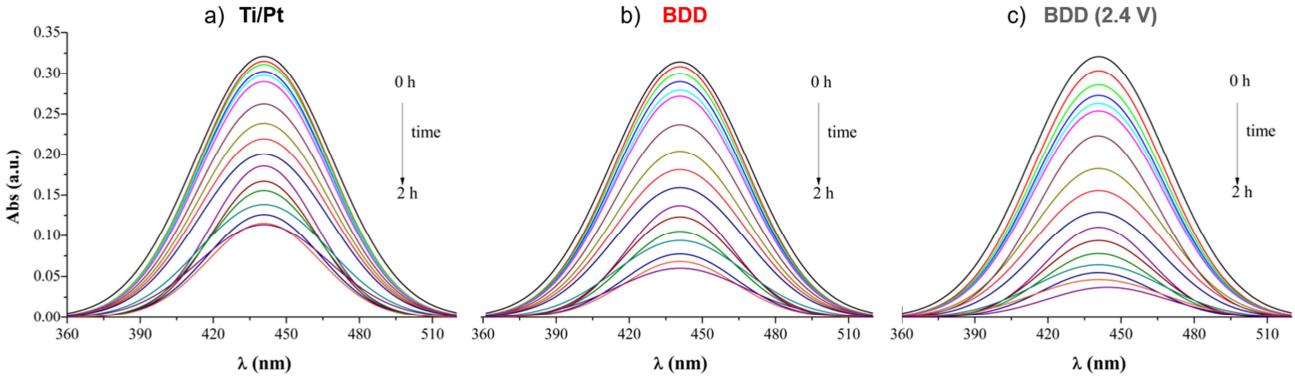

Figure S6. UV absorption spectra of aqueous RNO (2 x 10^{-5} mol dm^{-3}) obtained at 5 min intervals during 2 h potentiostatic electrolysis with (a) Ti/Pt and (b) BDD at 1.7 V vs. Ag/AgCl/Cl^-(3 M); and (c) BDD at 2.4 V vs. Ag/AgCl/Cl^-(3 M).

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Tables and Figures

Table 1. Effect of the anode on the voltammetric oxidation charge (Q_{oxid}/Q_{blank}); apparent rate constant for $^{\bullet}$OH generation ($k_{app}(\cdot OH)$) at 1.7 V (vs. Ag/AgCl/3M KCl); pseudo zero-order and first-order rate constants and 5 h-removal efficiencies for diclofenac oxidation (k_0, k_1) and TOC removal (k_0', k_1'); and the mineralization current efficiency (MCE) at 2 h, in 0.5 M Na_2SO_4.

	CV	$^{\bullet}$*OHs*	Diclofenac oxidation (UV)			TOC removal			
Electrode	Q_{oxid}/Q_{blank}	$k_{app}(\cdot OH)$ (min^{-1})	Eff_{Diclof} (%)	$10^8\ k_0$ (mol m^{-3} s^{-1})	$10^5\ k_1$ (s^{-1})	Eff_{TOC} (%)	$10^4\ k_0'$ (mol m^{-3} s^{-1})	$10^5\ k_1'$ (s^{-1})	MCE (%)
Ti/Pt	1.05	0.0088	70	5.34	6.12	33	8.49	1.00	2.7
BDD	20.8	0.0132/ 0.0161 [a]	100 [b]	41.2	80.9	100	25.56	71.40	9.9
Ti/SnO_2-Sb	1.45	0.0130	83	5.44	9.36	38	10.41	0.95	3.1
Ti/SnO_2-Sb-Pt(3%)	1.72	0.0113	90	7.29	11.7	53	12.32	1.96	4.0
Ti/SnO_2-Sb-Pt(13%)	1.76	0.0110	91	10.2	12.7	61	15.82	2.51	5.1

[a] $k_{app}(\cdot OH)$ (min^{-1}) calculated at 2.4 V (vs. Ag/AgCl/3M KCl)

[b] Eff_{Diclof} (%) after 1 h electrolysis

Figure 1. Scheme of (a) the electrochemical cell and (b) experimental set-up for the in-situ UV spectroelectrochemical measurements.

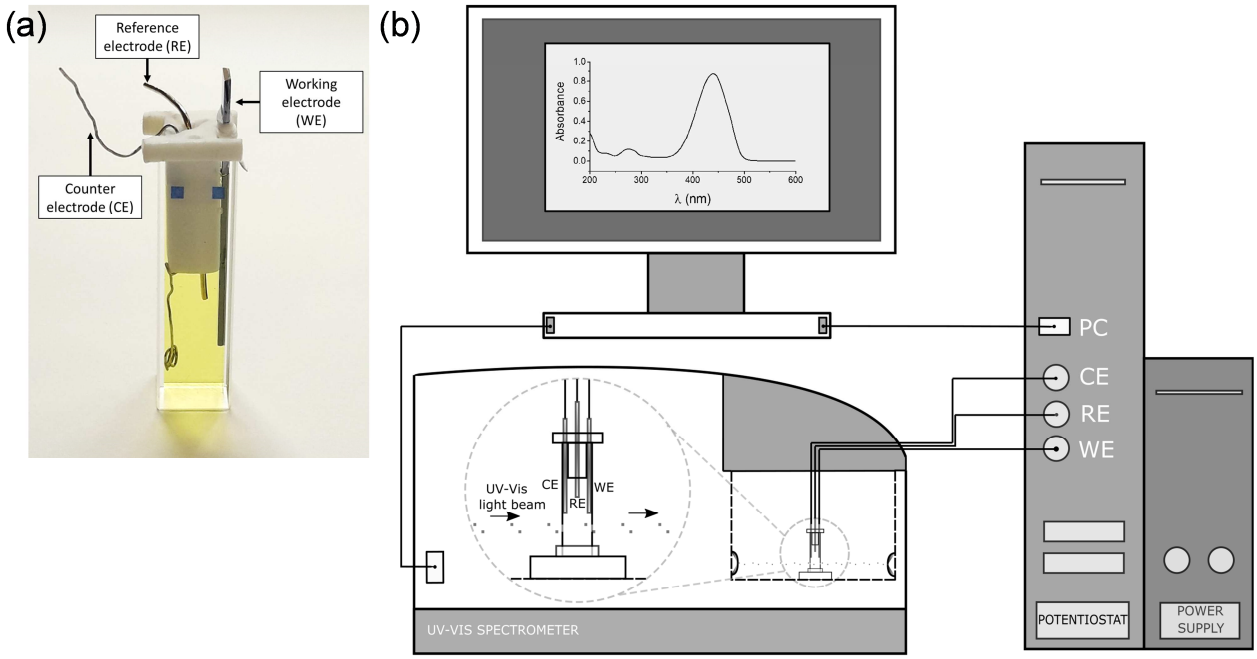


Figure 2. Cyclic voltammograms of (a) Ti/Pt and (b) BBD commercial anodes and those of (c-e) synthesized Ti/SnO_2-Sb-Pt(x) with x = 0 (c), 3 (d) and 13 (e) at.% Pt electrodes in the absence or presence of 200 ppm diclofenac. Electrolyte = 0.5 M Na_2SO_4. Refence electrode Ag/AgCl/3M KCl.

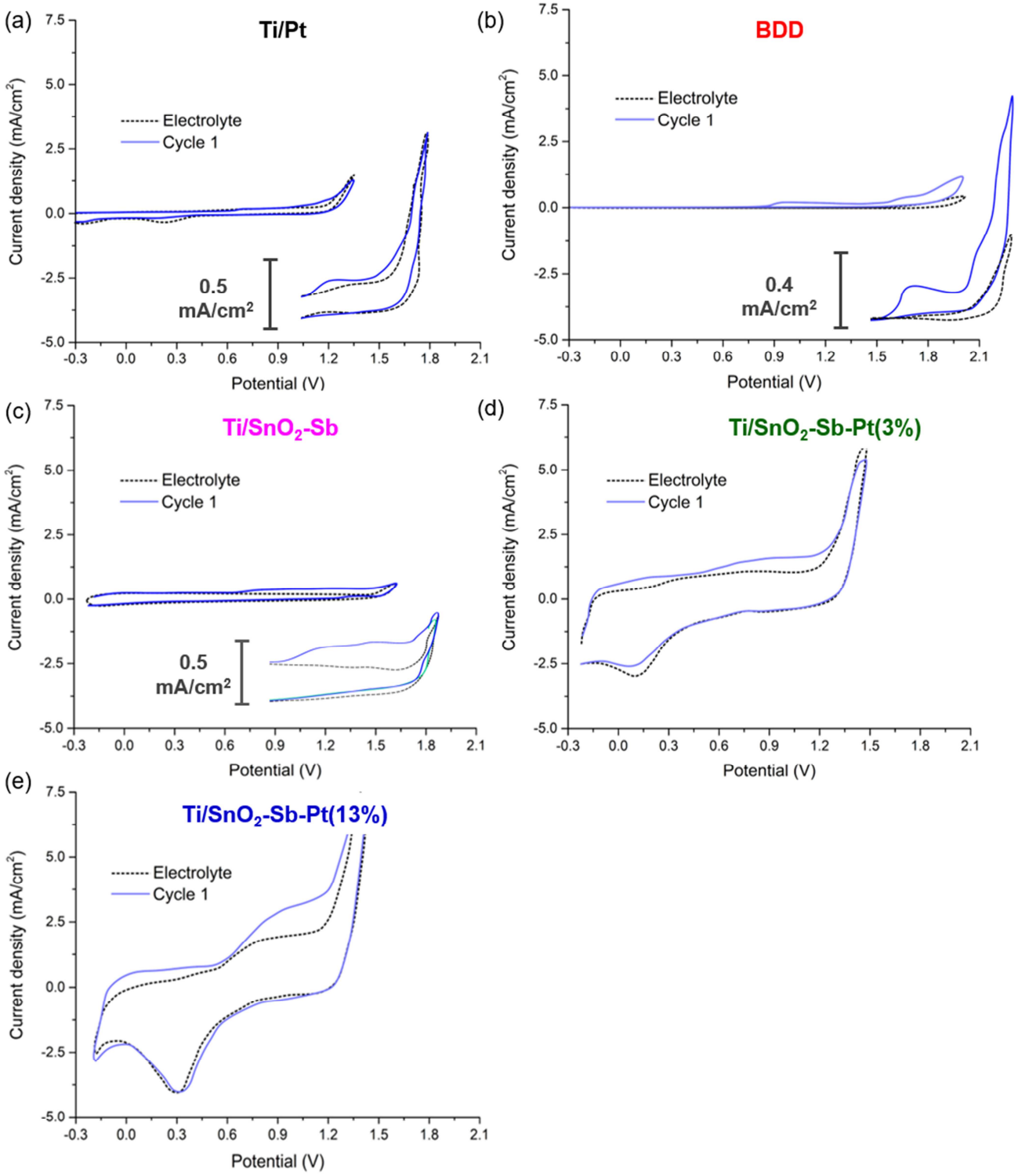


Figure 3. (a-c) UV absorption spectra of aqueous RNO (2 x 10^{-5} mol dm^{-3}) obtained at 5 min intervals during 2 h potentiostatic electrolysis with different SnO_2-Sb anodes at 1.7 V (vs. Ag/AgCl/3M KCl); and (d) the pseudo-first order kinetics (linear plots) of RNO degradation for determination of the apparent rate constant (k_{app}) for $^{\bullet}$OHs generation on the different anodes.

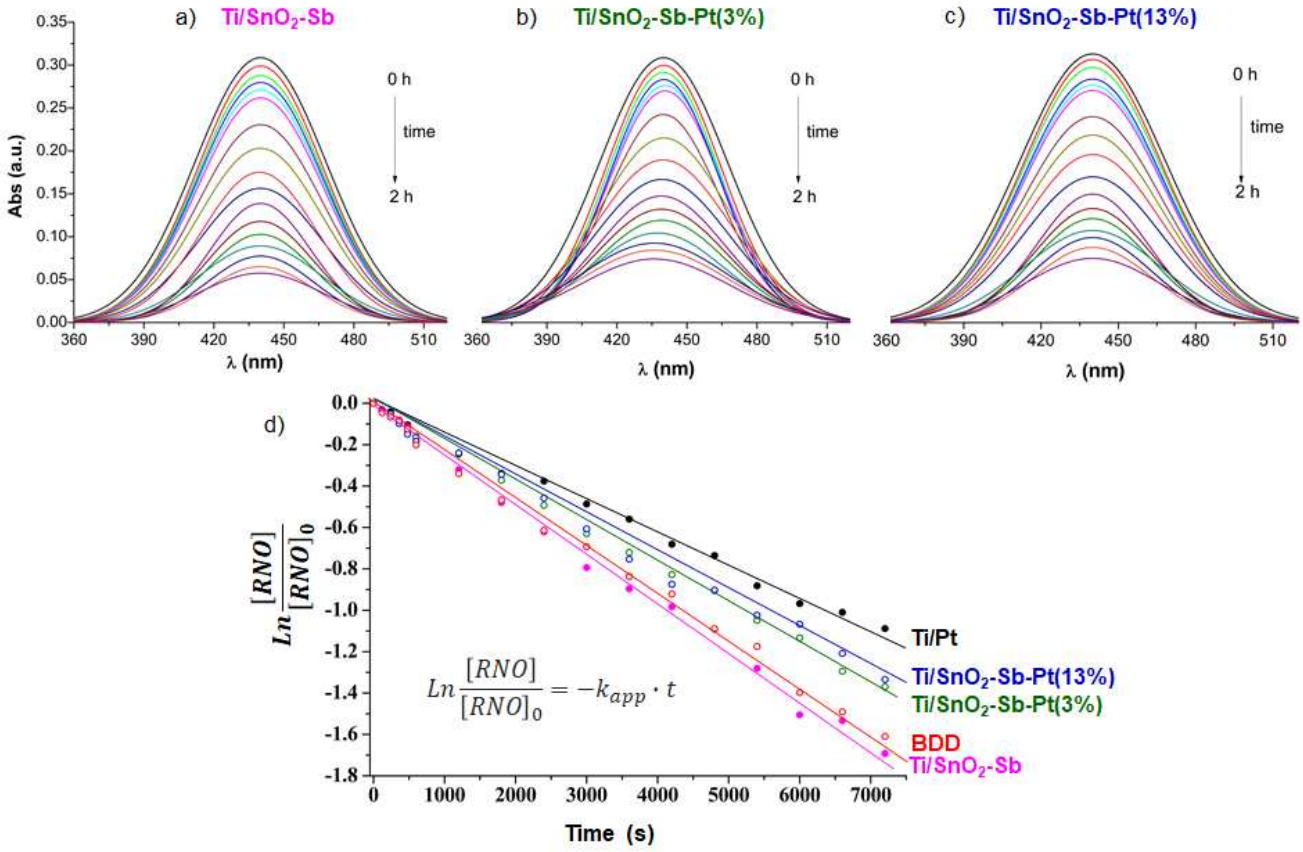


Figure 4. Evolution of diclofenac UV spectrum with time during the galvanostatic oxidation of a 200 ppm sodium diclofenac + 0.5 M Na_2SO_4 aqueous solution with different anodes. j = 50 mA cm^{-2}.

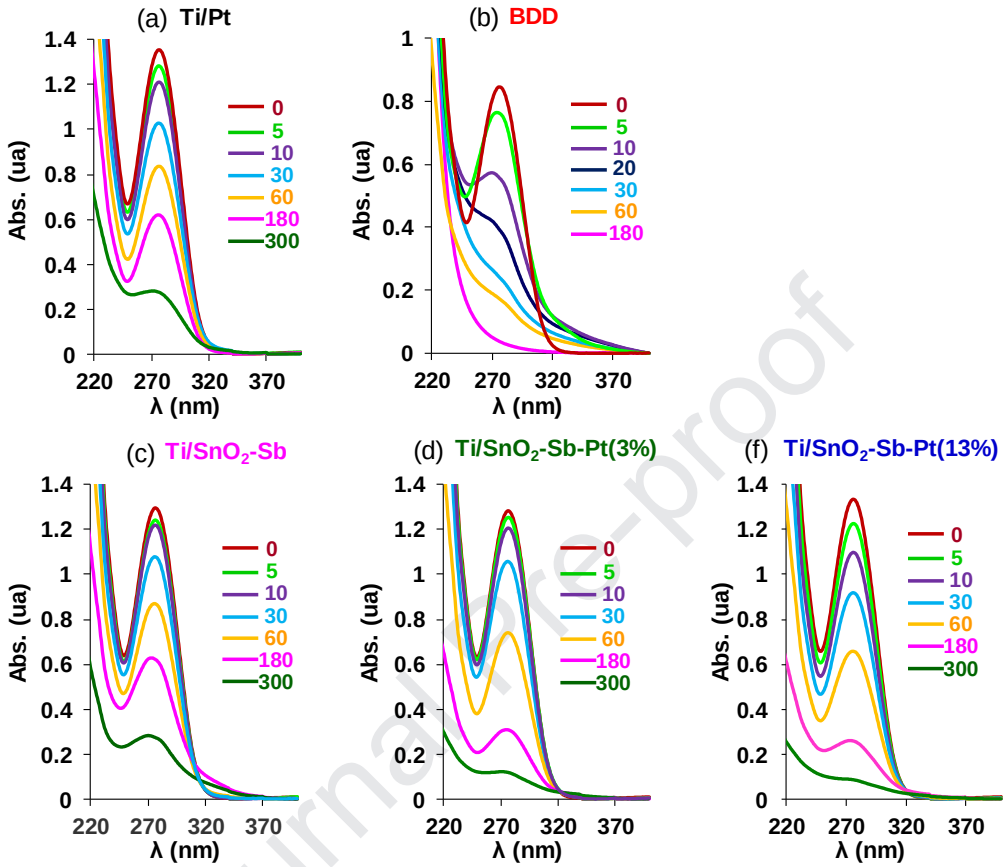
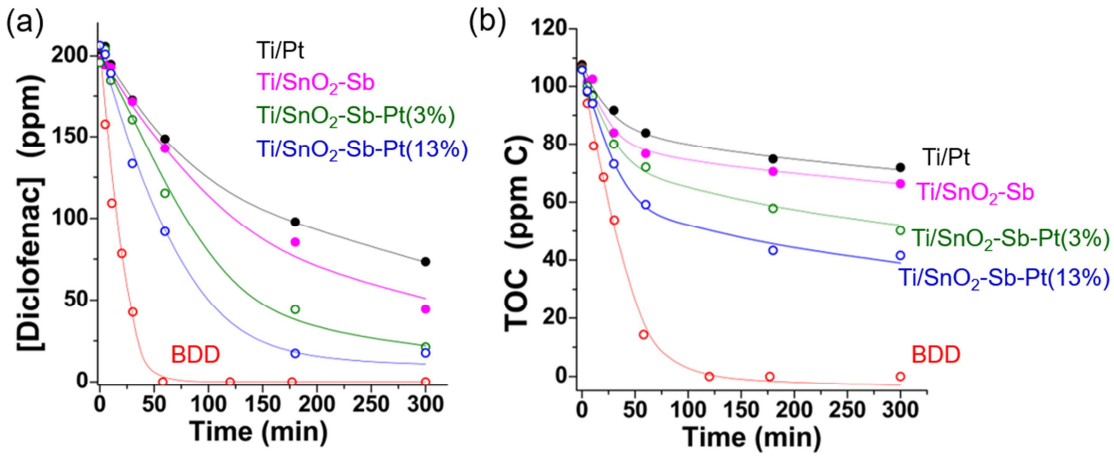


Figure 5. Evolution of the (a) diclofenac concentration (from UV) and (b) COT with time for the different anodes during the galvanostatic treatment at 50 mA cm^{-2}. Electrolyte = 200 ppm diclofenac + 0.5 M Na_2SO_4.



Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: