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Evidence of the electrochemical production of persulfate at TiO<sub>2</sub>-

nanotubes decorated with PbO<sub>2</sub>

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ABSTRACT: It is well-known that PbO <sub>2</sub> -based electrodes are considered as non-active	<b>D</b>		
anodes, producing higher concentrations of hydroxyl radicals in aqueous solutions, and	C C		
consequently, favouring the electrochemical degradation of organic pollutants.	0 L		
However, no evidences have been reported about the production of persulfates by	បា		
using this kind of electrodes in sulphate aqueous solutions. For this reason, the aim of	Ç		
this work is to prepare by electrochemical procedure (anodization and	nc		
electrodeposition) and characterize (by X-ray diffraction, scanning electron microscopy	<b>P</b>		
and potentiodynamic measurements) Ti/TiO <sub>2</sub> -nanotubes/PbO <sub>2</sub> disk electrodes (65 $\text{cm}^2$			
of geometrical area) to evaluated the electrochemical production of persulfate in	Z		
$Na_2SO_4$ solution as support electrolyte by applying 7.5 and 60 mA cm <sup>-2</sup> as well as the			
influence of electrosynthesis of hydroxyl radicals, in concomitance. Results clearly			

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showed that, a significant production of hydroxyl radicals and persulfate is achieved at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub>, but it depends on the current density. The production of \*OH at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> surface in Na<sub>2</sub>SO<sub>4</sub> solution was confirmed by RNO spin trapping reaction. The results were compared with Ti/Pt electrode to understand the effect when lower amount of \*OH is produced at active anode surface. Based on the results, Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> anode could exhibit good electrocatalytic properties for environmental applications involving persulfate oxidant.

35 Keywords: TiO<sub>2</sub> nanotubes; Persulfate; Hydroxyl Radical; PbO<sub>2</sub> electrodeposition

#### 36 1. INTRODUCTION

37 Advanced oxidation processes (AOPs) emerge as an alternative due to their 38 efficiency in oxidizing a wide variety of organic contaminants by the in-situ generation of highly oxidative species, <sup>1-4</sup> such as hydroxyl radicals ( $^{\circ}OH$ )<sup>1</sup>, persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) and 39 40 sulfate radical (SO4<sup>•-</sup>). Recently, <sup>•</sup>OH and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/SO<sub>4</sub><sup>•-</sup>-based advanced oxidation 41 processes (AOPs) have attracted extensive attention for degradation of persistent 42 organic contaminants in waters and wastewaters.<sup>1,2</sup> Metal ions and photochemical 43 radiation are the common methods to produce "OH and SO4" by activation of their 44 precursors. For this reason, the development of efficient activation approach is an important target.<sup>5-7</sup> In this frame, electrochemical technology has drawn increasing 45 attention in recent years<sup>4,8</sup> as a promising green tool with electrons acting as the green 46 47 reactant to produce/activate this class of oxidants.

Anodic oxidation (AO) is the most used approach to produce  $^{\circ}$ OH via electrolysis of water to O<sub>2</sub> at an anode (M) with high O<sub>2</sub>-overpotential to generate, physically or chemically, adsorbed hydroxyl radical M( $^{\circ}$ OH) as intermediate (reaction (1))  $^{8-11}$ . Published on 01 March 2018. Downloaded by University of Frankfurt on 05/03/2018 11:33:20

52 
$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^-$$
 (1)

53 Meanwhile,  $S_2O_8^{2-}$  and  $SO_4^{\bullet-}$  oxidants can be also electrochemically produced 54 via indirect AO of sulphate (equation 2) or indirect oxidation via  $^{\bullet}OH$  (equation 3 and 55 4).<sup>8,9,12, 13</sup>

56 
$$2SO_4^{2^-} \rightarrow S_2O_8^{2^-}$$
 (2)

57 
$$SO_4^{2-} + OH \to SO_4^{-0} + H_2O$$
 (3)

$$58 \qquad \mathrm{SO_4}^{-\bullet} + \mathrm{SO_4}^{-\bullet} \to \mathrm{S_2O_8}^{2^-} \tag{4}$$

59 However, the production or activation of these strong oxidants is not feasible at all electrodes and as it is well-known<sup>1,4,8,14</sup> this mainly depends on the nature of 60 electrocatalytic material. Among the anodes tested, boron-doped diamond (BDD) 61 electrode is preferred to produce electrochemically °OH, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and SO<sub>4</sub><sup>•-</sup>.<sup>15-26</sup> In the 62 case of \*OH, the weak BDD-\*OH interaction and greater O2 overpotential endorses the 63 64 generation of higher amounts of reactive physisorbed BDD(\*OH) radicals that mineralise more effectively organic pollutants than other anodes.<sup>8,9,11,13</sup> Meanwhile, the 65 in situ electrogeneration of  $S_2 O_8^{2-}$  and  $S O_4^{-}$  using BDD anode was well-established in 66 recent years.<sup>4,12</sup> Non-radical oxidation mechanism was generally proposed for 67 68 electrochemical production (equation 2). But sulphate can also react with <sup>•</sup>OH at BDD anode surface to generate  $SO_4^{\bullet-4}$ . 69

Pt anodes have been typically used as anodes for persulfate production by sulphate-electrolysis.<sup>5,14</sup> However, based on the existing literature,<sup>4,9,11,13</sup> BDD anodes have been preferentially investigated to produce  ${}^{\circ}OH$ ,  $S_2O_8{}^{2-}$  and  $SO_4{}^{\circ-}$  oxidants. Nevertheless, Pt is good electrocatalyst for oxygen evolution reaction, limiting an efficient production of hydroxyl radicals or persulfate on its surface, for this reason, a depressor for oxygen evolution is frequently added.<sup>5,14</sup> Meanwhile, the material acquisition cost of BDD anodes and their higher energy consumption incentivize the
 use of alternative cheaper materials <sup>8,11,19</sup>. For this reason, the research about the
 performance of other non-active electrodes for producing persulfate, such as SnO<sub>2</sub> and
 PbO<sub>2</sub>, could be very interesting.

80 Among the non-active anodes, PbO2-based electrodes clearly emerges as an 81 attractive electrocatalytic material due to its high oxygen evolution potential, low price, 82 relatively stable under the high positive potentials required, stability at high temperatures and ease of preparation.<sup>27</sup> Nevertheless, a common disadvantage when 83 84 PbO<sub>2</sub> electrodes are used for electrolytic approaches is that corrosion phenomenon can occur on anode surface dissolving Pb<sup>2+</sup> ions and pollute the solution, limiting its 85 applicability in some cases <sup>27</sup>. Therefore, the preparation of more stable PbO<sub>2</sub> anodes 86 87 is the aim of recent investigations in order to increase its economic value and 88 accelerate the practical applications of PbO<sub>2</sub> electrodes. In this way, some research 89 groups have proposed TiO<sub>2</sub> nanostructured materials, such as nanotubes, nanorods and nanowires, as support to deposit PbO2<sup>28-35</sup>. The unique properties of high aspect 90 91 ratio of TiO<sub>2</sub> nanostructured materials include large surface area, high cation 92 exchangeability, high catalytic activity, easier separation and recyclability. Then, the 93 use of nanotubes TiO<sub>2</sub> is an option that can improve the characteristics of PbO<sub>2</sub> 94 electrodes, such as long term stability and high corrosion resistance.<sup>36</sup>

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95 Therefore, the aim of this work is to study the viability of the use of TiO<sub>2</sub> 96 nanotubes arrays decorated with PbO<sub>2</sub> to produce electrochemically persulfate. Also, 97 the effect of hydroxyl radicals and hydrogen peroxide formation during persulfate 98 production was investigated, at different applied current densities. Finally, the 99 performances of Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> were compared with active anode (Ti/Pt), 100 without oxygen evolution depressor, to understand the differences during persulfate 101 electro-synthesis. Published on 01 March 2018. Downloaded by University of Frankfurt on 05/03/2018 11:33:20

#### 102 2. EXPERIMENTAL

#### 103 **2.1. Chemicals and Materials**

104 Methanol (vetec), ethanol (sigma-aldrich), acetone (anidrol), glycerol (vetec), 105 sodium sulfate, and sodium fluoride (NaF) were purchased from Anidrol, Brazil. All 106 solutions were prepared with high purity water obtained from a Millipore Milli-Q system 107 with resistivity >18 M $\Omega$  cm at 25°C.

#### 108 2.2. TiO<sub>2</sub> nanotubes Array and Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> Preparation

109 The TiO<sub>2</sub> nanotube array on the surface of titanium metal disk (1.8 mm thick 110 and nominal surface area of 63.5 cm<sup>2</sup>) was grown by anodization method <sup>31</sup>. Prior to 111 anodization, the titanium metal plate was polished with abrasive paper and degreased 112 sonication in acetone, ethanol, and methanol, respectively. The titanium metal disk was 113 dried, and it was used as an anode while a stainless steel disk was employed as 114 cathode. The electrolyte was composed of a mixture of glycerol and ultrapure water in 115 a 1.3:1 ratio (v/v) containing 0.5 wt% NaF and 0.2 M Na<sub>2</sub>SO<sub>4</sub> as the support electrolyte 116 by applying 30 V for 2 h. After anodization, the surface was washed with deionized 117 water, dried, and calcined at 500°C for 1.5 h under air atmosphere. The 118 electrodeposition of PbO<sub>2</sub> onto a Ti/TiO<sub>2</sub>-nanotubes disk array was achieved using a 119 galvanostatic method by using a solution of 0.25 M Pb(NO<sub>3</sub>)<sub>2</sub> + 0.1 M HNO<sub>3</sub> by applying 30 mA cm<sup>-2</sup> during 10 min at  $25^{\circ}$ C. 120

## 121 2.3. Surface characterization of Surface TiO<sub>2</sub> nanotubes and Ti/TiO<sub>2</sub> 122 nanotubes/PbO<sub>2</sub>

Surface morphology of Ti/TiO<sub>2</sub>-nanotubes and Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> deposits were characterized using a scanning electron microscope (SEM, TESCAN VEGA model 3SBH), and X-ray diffractometer (DRX 6100 SHIMADZU) using Cu Ka ( $\lambda$ =1.54 Å) radiation. Electrochemical measurements were carried out using an AutoLab 302N (Metrohm workstation).

#### 128 2.4. Electrochemical Measurements

129 For the study of electrochemical characteristics of Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub>, 130 polarization measurements were performed in 0.05 M Na<sub>2</sub>SO<sub>4</sub> between 0.3 and 4 V vs Ag/AgCl (3M) at 50 mV s<sup>-1</sup>. A comparison with Pb/PbO<sub>2</sub> and Ti/Pt electrodes was also 131 132 performed. The three-electrode cell was constituted by Pb/PbO<sub>2</sub>, Ti/Pt or Ti/TiO<sub>2</sub>-133 nanotubes/PbO<sub>2</sub> (1 cm<sup>2</sup> of exposed area), Ag/AgCl (KCl 3 M) and Pt wire, as working, 134 reference and counter electrodes, respectively. Bach experiments were also performed 135 for salicylic acid-trapping hydroxyl radicals by using a 200 mL-cell with Tacussel model 136 PJT24-1 potentiostat-galvanostat at 25°C with 0.025M of Na<sub>2</sub>SO<sub>4</sub> as supporting 137 electrolyte. Ti/Pt or Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> was used as anode (1 cm<sup>2</sup>), and a 138 stainless steel plate was used as cathode.

#### 139 2.5. Electro-synthesis of oxidants

Electrochemical experiments were performed using an electrolytic flow cell with a single compartment with parallel plate electrodes with nominal surface area of 63.5  $cm^2$  (Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> or Ti/Pt as anode and stainless steel as cathode) for 1 L of solution (Fig. 1). Different current densities (ranging from 7.5 to 60 mA cm<sup>-2</sup>) were 144 used in 0.05 M of Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte for assessing the production of 145 hydroxyl radicals and persulfate. In the case of persulfate concentration, the effect of 146 concentration of sulphate in the solution was studied when Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> 147 was used.

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151 Figure 1. a: 1) anodic part; 2) electric support to anode; 3) anode (Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> or Ti/Pt); 4) reaction compartment, 5) cathode (stainless steel disk); 6) metallic support to electrical 152 153 contact with cathode and 7) cathodic part. B) electrochemical system: 1) reservoir, 2) 154 thermometer, 3) electrochemical cell and 4) peristaltic pump. C: image of electrochemical cell 155 with each one of its compartments assembled.

#### 156 2.6. Analytical Methods

157 Hydroxyl radicals were detected by the bleaching of N.N-dimethyl-4-158 nitrosoaniline (RNO). The originally yellow solution was decolorized through reaction between RNO and <sup>•</sup>OH forming an adduct <sup>37,38</sup>. The bleaching of the 2×10<sup>-5</sup> M RNO 159 160 solution in 0.05 M Na<sub>2</sub>SO<sub>4</sub> was followed by spectrophotometry using an Analytik Jena 161 Specord 210 Plus UV/Vis spectrophotometer in 440 nm. For persulfate quantification 162 was performed by the spectrophotometric ISCO methodology proposed by Liang et al. (2008) <sup>39</sup>. Samples were analyzed for determining the concentration changes of 163



- salicylic acid and by-products by HPLC. More details about the salicylic acid-trapping
- 165 hydroxyl radicals method can be found elsewhere.<sup>40</sup>

#### 166 3. RESULTS AND DISCUSSION

#### 167 **3.1. Surface analysis of Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub>**

168 Ti/TiO<sub>2</sub>-nanotubes were successfully synthesized in solution of glycerol and 169 ultrapure water containing with NaF and Na<sub>2</sub>SO<sub>4</sub> by galvanostatic electrolysis with a 170 potential of 30 V for 2 h. The surface morphology of deposits was observed by SEM, 171 showing TiO<sub>2</sub> nanotubes with diameters of approximately 100-200 nm as observed in 172 the images (Fig 2). The TiO<sub>2</sub> nanotubes grow vertically on the substrate and form a 173 dense array (Fig. 2a). XDR measurements were also carried out at different spots (Fig. 174 3) showed that the composition corresponds to the anatase phase of TiO<sub>2</sub>, which demonstrates that the nanotubes were successfully synthetized.<sup>36</sup> 175



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Figure 2. (a) SEM images of anodized Ti/TiO<sub>2</sub>-nanotubes, (b) magnification of grown of Ti/TiO<sub>2</sub> nanotubes and their dimensions.



Figure 3. XRD spectrum from TiO<sub>2</sub> nanotubes showing that anatase phase is the predominant crystalline structure.

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185 On the other hand, PbO<sub>2</sub> crystals were successfully deposited onto Ti/TiO<sub>2</sub>-186 nanotubes arrays, according to SEM images (Fig. 4), by galvanostatic method at 30 mA cm<sup>-2</sup> during 10 min at 25°C. The PbO<sub>2</sub> deposit was composed of orderly arranged 187 188 tetragonal PbO<sub>2</sub> crystals. However, these tetragonal crystals can organize in tree form 189 when the electrodeposition time is increased, as already reported by Cerro-Lopez et al. 190 <sup>36</sup>. For this reason, the electrolysis time of 10 min is very important to obtain 191 homogenous PbO<sub>2</sub> deposit <sup>27, 36</sup> and it was chosen as experimental condition of our preparation work, based on the existing literature <sup>36</sup>. 192

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### Figure 4. SEM image of complete PbO<sub>2</sub> deposit into Ti/TiO<sub>2</sub>-nanotubes.

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197 The deposit of PbO<sub>2</sub> into the nanotubular structure of TiO<sub>2</sub> was confirmed by means 198 of XRD and SEM analyses. Fig. 5 shows the XRD pattern for a PbO<sub>2</sub> deposit during 10 199 min on the TiO<sub>2</sub> nanotubes, which exhibits the characteristic peaks of the Plattnerite 200 phase  $(\beta$ -PbO<sub>2</sub>)<sup>27</sup> in a tetragonal crystalline structure, confirming the success of deposit 201 formation.<sup>36</sup>



## **Figure 5.** XRD diffractogram for the PbO<sub>2</sub> deposit on TiO<sub>2</sub>-nanotubes array after 10 min of electrolysis time in a 0.25 M Pb(NO<sub>3</sub>)<sub>2</sub> + 0.1 M HNO<sub>3</sub> solution.

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205 **3.2. Electrochemical measurements** 

It is well established that oxygen evolution reaction (OER) results from reactions in series and hydroxyl radicals are one of the most important intermediates produced during it <sup>4, 9, 11</sup>. The first common step is the discharge of water molecules to hydroxyl radicals (Eq. 1). The following steps depend on the strength of the interaction between hydroxyl radicals and the electrode surface which, in turn, depends on the nature of the electrode material.

212 Two classes of materials can be distinguished: "active" or "non-active" 213 electrodes <sup>4, 8, 9, 11</sup>. In the former case, a strong interaction with hydroxyl radicals exists 214 and the oxygen evolution reaction occurs via the formation of higher oxides, while, in 215 the latter, the substrate does not participate in the process and the oxidation is assisted 216 by hydroxyl radicals that are weakly adsorbed at the electrode surface. Then, prior to 217 electro-synthesis experiments and on the basis of the electrocatalytic nature of each 218 one of the electrodes used, electrochemical measurements were performed to increase 219 the understanding of the production of oxidants. Figure 6 shows linear polarization 220 curves in 0.05 M Na₂SO₄ solution at 25°C registered at a scan rate of 10 mV s<sup>-1</sup> for 221 Ti/Pt, Pb/PbO2 and Ti/TiO2-nanotubes/PbO2 electrodes (Pb/PbO2 was used as 222 comparative material). The curves are very different from one another and show that 223 oxygen evolution potential depends on the electrocatalytic material; 1.24 V, 1.9 V and 2.2 V versus Ag/AgCl (3.0 M) for Ti/Pt, Pb/PbO2 and Ti/TiO2-nanotubes/PbO2, 224 225 respectively. Ti/Pt exhibited a low oxygen evolution overpotential starting near of 1.10 226 V increased slightly to 1.24 V where oxygen evolution becomes more apparent <sup>41,42</sup>. 227 This low potential makes that Ti/Pt be a good electrocatalysts for the oxygen evolution 228 reaction (Eq. 5); while Pb/PbO<sub>2</sub> and Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> have high oxygen 229 evolution overpotential, and consequently are a poor electrocatalysts for the OER (it of Tafel slope was estimated (data not shown), and these were

for all electrodes (1.46, 1.28 and 1.22 V decade<sup>-1</sup> for Ti/TiO<sub>2</sub>-

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Ti/Pt Pb/PbO<sub>2</sub> Ti/TiO2-nanotubes/PbO2 1.0×10 Current / A 7.5×10-3 5.0×10-3 2.5×10-3 0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 Potential / V vs Ag/AgCI

230 starts at 1.65 V, increasing more strongly over 1.85 V for Pb/PbO<sub>2</sub> and 2.1 V for 231 Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> (Fig. 6)).<sup>41,42</sup>

232  $^{\bullet}OH \rightarrow \frac{1}{2}O_{2} + H^{+} + e^{-}$ (5)

23 t, the electrogenerated hydroxyl radicals can be involved in the 24 rting electrolyte (Eqs. 2 to 4) in the proximity of anode surface, and, 24 evolution. However, in the case of Pt-supported on Ti electrode, Tafel 24 ed in two segments, which may indicate that, two main reactions are 24 anode (\*OH and O<sub>2</sub>) at current densities below 30 mA cm<sup>-2</sup>. 24 eaction is favoured at Pb/PbO2 and Ti/TiO2-nanotubes/PbO2 anodes, 24 experimental information discussed above, the production of "OH is 24 on the surface, before the oxygen evolution.

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Figure 6. Polarization curves at different electrodes obtained in 0.05 M Na<sub>2</sub>SO<sub>4</sub> with a scan rate of 10 mv s<sup>-1</sup>. Electrode area: 1 cm<sup>2</sup>.

This behaviour indicates that Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> could exhibit good electrocatalytic properties for production of oxidants as well as for degradation of organic pollutants, due to a low adsorption of oxidizing species generated on the surface <sup>19, 41, 42</sup>. For this reason, its comparison was carried out with Pt anode in order to avoid the drawbacks achieved when PbO<sub>2</sub> is used.<sup>3,27,41</sup>

#### 256 **3.3. Electro-generation of hydroxyl radicals**

Hydroxyl radicals formed by water discharge at Ti/Pt and Ti/TiO<sub>2</sub> nanotubes/PbO<sub>2</sub> electrodes (Eq. 6) can be detected using UV-visible measurements.

$$259 \quad H_2O \rightarrow {}^{\bullet}OH + H^+ + e^- \tag{6}$$

The indirect technique for the detection of low concentrations of hydroxyl radicals is carried out by trapping these radicals via an addition reaction (spin trapping) in order to produce a more stable radical (spin adduct). In this work, p-nitrosodimethylaniline (RNO) was used as spin trap (Eq. 7). It is important to remark that this technique is reliable to determine qualitatively the formation of hydroxyl radicals,<sup>37</sup> even when other trapping species can be used.<sup>38</sup>



267 The use of this particular spin trap is particularly advantageous because under 268 these conditions of concentration and pH, it is electrochemically inactive. Moreover, the addition reaction occurs at a very high rate constant  $(1.3 \times 10^{10} \text{ M}^{-1} \text{s}^{-1})^{37, 43}$  and hence is very selective. Figure 7 shows the adsorption spectrum of aqueous RNO solution  $(2 \times 10^{-5} \text{ M})$  during galvanostatic electrolysis at Ti/Pt and Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> electrodes by applying 7.5 and 60 mA cm<sup>-2</sup>. These current densities were chosen to understand the behaviour at lower and higher electrical conditions.<sup>41-45</sup>

As can be observed from Fig. 7, a different decrease in optical density at 440 nm during electrolysis is attained at both electrocatalytic materials under different current densities. For example, at 7.5 mA cm<sup>-2</sup>, absorbance quickly decreased at Ti/Pt (Fig. 7c), as a function of time; while a slower disappear of band is observed at Ti/TiO<sub>2</sub>nanotubes/PbO<sub>2</sub> (Fig. 7a) under similar experimental conditions. This result seems to indicate that, Ti/Pt anode produces higher concentrations of hydroxyl radicals on its surface, and these react with RNO to form the adduct.





**Figure 7.** Adsorption spectra of aqueous RNO solution  $(2 \times 10^{-5} \text{ M})$  obtained at different electrolysis-time intervals under galvanostatic conditions at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> (a, b) and Ti/Pt (c, d) electrodes by applying 7.5 mA cm<sup>-2</sup> (a, c) and 60 mA cm<sup>-2</sup> (b, d) at 25°C.

However, the UV-vis spectrum showed the existence of intermediates that absorb irradiation approximately at 245 and 323 nm, which were not observed at Ti/TiO<sub>2</sub>-

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288 nanotubes/PbO<sub>2</sub> electrode during electrolysis by applying 7.5 mA cm<sup>-2</sup>. Similar 289 behaviour was attained at 60 mA cm<sup>-2</sup>. These results clearly demonstrated that, •OH 290 radicals could react with RNO to form adduct species, but, RNO and adduct are rapidly oxidized on Ti/Pt surface, producing intermediates.<sup>33</sup> Meanwhile, for Ti/TiO<sub>2</sub>-291 292 nanotubes/PbO<sub>2</sub> anode, there is accumulation of \*OH radicals on its surface, promoting only the formation of adduct.<sup>31</sup> In fact, no absorption bands were achieved at 245 and 293 294 323 nm. Then, generally speaking, these figures confirm that the nature of the 295 electrocatalytic material plays an important role in the electrochemical production of 296 significant concentrations of 'OH radicals, but their concentration also depends on the 297 applied current density used. This effect is more evident when the evolution of 298 normalized absorbance values is plotted as a function of time (Fig. 8), indicating that 299 Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> anode produces efficiently <sup>•</sup>OH radicals. These results are in agreement with the proposed model by Comninellis<sup>37</sup> in which the PbO<sub>2</sub> electrocatalytic 300 301 material is considered a non-active anode due to the significant production of 'OH 302 radicals, physically adsorbed.



Figure 8. Normalized absorbance decay of RNO solution as consequence of hydroxyl radicals electrogeneration at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> (a) and Ti/Pt (b) electrodes by applying 7.5 and 60 mA cm<sup>-2</sup> during electrolysis in 0.05 M Na<sub>2</sub>SO<sub>4</sub> at 25°C.

308 By using salicylic acid-trapping method,<sup>40</sup> electrochemical oxidation of 100 mg L<sup>-1</sup> of 309 salicylic acid, at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> or Ti/Pt, by applying 7.5 and 60 mA cm<sup>-2</sup> in 310 sulphate-supporting electrolyte showed that salicylic acid is converted to 2,3-dihydroxy 311 benzoic acid (2,3-DHBA); 2,5-dihydroxy benzoic acid (2,5-DHBA); and catechol (CT)). 312 In the case of Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> anode, higher concentrations of 2,3-DHBA and 313 2.5-DHBA, preferentially, were produced; 36 and 15 mg L<sup>-1</sup>, respectively, after 60 min. 314 Meanwhile, at Ti/Pt, insignificant amounts of CT, 2,3-DBHA and 2,5-DBHA were 315 detected (minor than 2.5 mg L<sup>-1</sup>). The rate of salicylic acid is faster due to the reactivity 316 of \*OH formed at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> surface. The formation of 2,3-DBHA and 2,5-317 DBHA occurs with the organic molecules in the proximity of the surface layer of 'OH 318 and via homogeneous reaction between the organic molecules and the •OH confined 319 within a reaction cage nearby the electrode surface. But, at Ti/Pt, no enough 320 concentration of "OH is present in its surface, avoiding the evolution of higher 321 concentration of aromatics compounds and increasing the rate of direct oxidation 322 mechanism. These results clearly confirm the production of hydroxyl radicals at both 323 electrocatalytic materials in different amounts.

However, the main goal of our investigation is to show that, the electrogeneration of persulfate is feasible at  $Ti/TiO_2$ -nanotubes/PbO<sub>2</sub> anode, and the understanding the effect of hydroxyl radicals in its formation. In this context, the results reported until now have confirmed the efficacy of  $Ti/TiO_2$ -nanotubes/PbO<sub>2</sub> anode to produce hydroxyl radicals, but the formation of other oxidants, such as  $H_2O_2$  (equations 8 and 9) and persulfates (equations 2, 3 and 4) must be verified by using Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte.<sup>44</sup>

331 In the case of  $H_2O_2$ , it is a powerful oxidant that can be formed through water oxidation 332 by either a direct or an indirect mechanism. For this reason, its determination is useful 333 to better clarify the role of generated oxidizing agents.

$$334 \qquad 2H_2O \to H_2O_2 + 2H^+ + 2e^- \tag{8}$$

 $335 \quad 2^{\bullet}OH \rightarrow H_2O_2 \tag{9}$ 

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However, no significant concentrations were measured by applying different 336 337 current densities at both anode materials. This behaviour can be related to the 338 competition between the formations of free hydroxyl radicals/persulfates with hydrogen peroxide at both anodes because higher concentration <sup>•</sup>OH radicals and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> may be 339 340 produced and consequently, it does not allow the production of H<sub>2</sub>O<sub>2</sub>.<sup>44</sup> Another 341 important feature is that, it is also expected that after formation, hydrogen peroxide can 342 be decomposed through oxidation at the electrode surface (equation 10), limiting its 343 presence in the solution.

$$344 \quad H_2O_2 \to O_2 + 2H^+ + 2e^- \tag{10}$$

In the case of persulfate, based on the existing literature  $^{4,10-11,16,18,19,22,41,42}$  its formation occurs in sulphate medium due to the oxidation of the sulfuric acid or sulphate in solution. To evaluate the amount of persulfate formed during water oxidation in Na<sub>2</sub>SO<sub>4</sub>, bulk electrolyzes at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> and Ti/Pt electrodes by applying different current densities (7.5, 15, 30 and 60 mA cm<sup>-2</sup>) were performed. The concentration of persulfate was determined in the anolyte by ISCO method.

Figure 9 shows the influence of current density on the  $S_2O_8^{2-}$  concentration. As can be observed, significant differences were attained at both electrocatalytic materials. At Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> anode, an increase on the  $S_2O_8^{2-}$  concentration is achieved when an increase on the applied current density is achieved. Conversely, when higher current density is applied at Ti/Pt, lower persulfate concentration is produced.



**Figure 9.** Electrosynthesis of  $S_2O_8^{2^-}$  at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> (a) and Ti/Pt (b) electrodes by applying different applied current densities in 0.05 M Na<sub>2</sub>SO<sub>4</sub> at 25°C.

In the former case, a gradual increase on the amount of hydroxyl radicals produced is attained at different applied current densities, favouring the reaction between  ${}^{\circ}OH$  and SO<sub>4</sub><sup>2-</sup> in the Nernst layer at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> anode, and consequently, producing efficiently persulfate. In fact, when faradaic efficiencies (fE) were estimated, these values increase when the current density increases, however, no higher fE were obtained (0.14%; 0,065%; 0,054% and 0,045% by applying 7.5, 15, 30 and 60 mA cm<sup>-</sup>

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<sup>2</sup>, respectively at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub>) which indicate that other parasite reactions 367 368 are being favoured. Meanwhile, at Pt-supported on Ti electrode, the higher is the 369 current density, the higher is the oxygen evolution (equation 5). In effect, fE values are 370 minor than those obtained at Ti/TiO2-nanotubes/PbO2 anode, confirming that this 371 material spent the electrical energy promoting the oxygen evolution reaction (0,14%; 0,062%; 0,0087% and 0,0012% by applying 7.5, 15, 30 and 60 mA cm<sup>-2</sup>, respectively at 372 373 Ti/Pt)). These results in agreement with the production of hydroxyl radicals reported in 374 Fig. 7. In fact, these reactions explain the rapid decrease of RNO absorbance spectra 375 at Ti/Pt when Na<sub>2</sub>SO<sub>4</sub> is used as supporting electrolyte because this electrode favours 376 the electrogeneration of persulfate, consuming RNO by parallel reactions (direct to 377 anode surface or persulfate-mediated oxidation) instead of favouring the rapid 378 formation of adduct. Conversely, the heterogeneous production of hydroxyl radicals at 379 Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> surface is the main reaction attained, and after that, the 380 formation of persulfate is involving homogenous catalytic reaction:

381 
$$\text{TiO}_2\text{-nanotubes/PbO}_2(^{\bullet}\text{OH}) + \text{SO}_4^{2^-} \rightarrow \text{TiO}_2\text{-nanotubes/PbO}_2(\text{SO}_4^{-\bullet}) + \text{OH}^-$$
 (11)

382 TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub>(SO<sub>4</sub><sup>-•</sup>) + SO<sub>4</sub><sup>2-</sup> 
$$\rightarrow$$
 S<sub>2</sub>O<sub>8</sub><sup>2-</sup> + e<sup>-</sup> (12)

383 It is interesting to note that, even when 14  $\mu$ M of persulfate is obtained at Ti/Pt 384 anode at 7.5 mA cm<sup>-2</sup> (more than the concentration obtained at Ti/TiO<sub>2</sub>-385 nanotubes/PbO<sub>2</sub> electrode at more higher current density), it is desirable that a 386 significant range of applied currents during the process in order to improve the 387 operating conditions (e.g.: temperature increase and concentration of sulphate) or no 388 use of oxygen reaction depressor.

A set of new experiments was performed to give more evidences about the formation of persulfate by homogeneous catalytic reaction, as previously proposed. Figure 10 shows the trends of  $S_2O_8^{2-}$  synthesized at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> anode by applying

60 mA cm<sup>-2</sup> at different concentrations of sodium sulphate at 25 °C. As can been see, 392 393 the higher is the sodium sulphate concentration, higher persulfate concentration is 394 produced, in according to the reactions 11 and 12. This behaviour confirms that, a 395 rapid production of persulfate is achieved at Ti/TiO2-nanotubes/PbO2 anode due to its 396 efficient production of hydroxyl radicals on its surface as well as the direct oxidation of 397 sulphate ion. Similar experiments were performed at Ti/Pt electrode, however, a slight 398 increase on the concentration of persulfate this behaviour is probably due to the 399 increase on the conductivity, which favoured the oxygen evolution reaction than the hydroxyl radicals and persulfate production.<sup>18</sup> 400



Figure 10. Electrochemical production of persulfate, as a function of time, with Ti/TiO<sub>2</sub> nanotubes/PbO<sub>2</sub> anode obtained by applying 60 mA cm<sup>-2</sup> at different concentrations of sodium sulfate.

Finally, the whole process is highly dependent on the mediated oxidation surface generation of intermediate  $TiO_2$ -nanotubes/PbO<sub>2</sub>(SO<sub>4</sub><sup>-•</sup>), which is more feasible than the direct electrochemical formation of  $S_2O_8^{2-}$  (equation 2). Additionally, it is important to consider that the decomposition of  $S_2O_8^{2-}$  to  $H_2O_2$  is feasible, reducing its oxidation power efficiency in the bulk solution, as mainly observed at Ti/Pt electrode (see Fig. 9b).

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413 In order to propose the use of Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> as anode for 414 producing electrochemically persulfate, its electrochemical stability was 415 evaluated by fixing a current density for prolonged electrolysis times. Fig. 11 416 shows that the variation of E<sub>appl</sub> as a function of time, revealing that no increase 417 in the values of E<sub>appl</sub> was achieved up to 120 h. This is due to the tetragonal 418 organized-array of the PbO<sub>2</sub> crystals which give high electrochemical stability 419 for long-term applications. Another interesting feature is that, no pollution of 420 Pb<sup>2+</sup> was detected after longer times of electrolysis with Ti/TiO2-421 nanotubes/PbO<sub>2</sub> anode, in contrast with the results achieved when  $Pb/PbO_2$ electrode is used. The release of Pb2+ was monitored by electroanalytical 422 measurements.46 423



424

Figure 11. Variation of E<sub>appl</sub> at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> anode, as a function of time, during
 fixed current densities values for prolonged electrolysis times.

#### 428 CONCLUSIONS

429 In summary, the large PbO<sub>2</sub> electrodes composed of orderly arranged TiO<sub>2</sub> 430 nanotubes were successfully synthesized via a simple, rapid, and efficient 431 electrochemical approach. Also, the study about the effect on the production of 432 hydroxyl radicals and persulfate was studied, for first time, at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> 433 anodes. Based on the results obtained, a significant amount of 'OH is produced at 434 Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> surface is achieved when  $Na_2SO_4$  is used as supporting 435 electrolyte (confirmed by RNO spin trapping reaction), in comparison with Ti/Pt. These 436 radicals play an important role in secondary reactions to the production of strong 437 oxidants (persulfate). In fact, an evaluation of the concentration of oxidants indicates 438 that Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> promotes the formation of hydroxyl radicals and persulfate 439 with lower amounts of hydrogen peroxide. At the same time, the concentration of 440 persulfate is improved by an increase on the applied current density as well as on the 441 sulphate concentration in solution. In light of these results, this study open new 442 considerations about the real mechanism followed to form  $S_2 O_8^{2-}$  species as well as we 443 can propose the use of  $Ti/TiO_2$ -nanotubes/PbO<sub>2</sub> anode for environmental applications, 444 such as anodic oxidation of organic pollutants.

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451

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