



## Research Paper

# Use of Sub-stoichiometric Titanium Oxide as a Ceramic Electrode in Anodic Oxidation and Electro-Fenton Degradation of the Beta-blocker Propranolol: Degradation Kinetics and Mineralization Pathway



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## ABSTRACT

Oxidative degradation of aqueous acidic solutions of the beta-blocker propranolol (PPN) has been studied by anodic oxidation (AO) and for the first time by electro-Fenton (EF) process using sub-stoichiometric titanium oxide (Ti<sub>4</sub>O<sub>7</sub>) anode elaborated by plasma deposition. The oxidative degradation of the PPN by Ti<sub>4</sub>O<sub>7</sub>(•OH) formed at the surface of the Ti<sub>4</sub>O<sub>7</sub> anode and •OH generated via electrochemically assisted Fenton's reaction was investigated. Decay of PPN concentration followed pseudo-first order reaction kinetics with degradation rates influenced by both applied current and initial PPN concentration. The absolute rate constant of the reaction between PPN and •OH/Ti<sub>4</sub>O<sub>7</sub>(•OH) was determined by competition kinetics and found to be  $(2.99 \pm 0.02) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ . Relatively high mineralization efficiency of PPN solution (82% TOC removal) was achieved by AO with Ti<sub>4</sub>O<sub>7</sub> anode at 120 mA after 480 min of treatment, whereas almost complete mineralization (96% TOC removal) was reached at similar conditions in EF process. Analogous EF treatment with DSA anode showed lower mineralization (89% TOC removal) compared to Ti<sub>4</sub>O<sub>7</sub> anode. The initial N content of PPN was mainly released as NH<sub>4</sub><sup>+</sup>, with smaller proportion of NO<sub>3</sub><sup>-</sup>. Aromatic intermediates such as 1-naphtol; hydroxylated 1-naphtol and phthalic acid were identified by both reversed-phase HPLC and GC-MS analyses. Oxalic, oxamic, maleic and glyoxylic acids were the main short-chain carboxylic acid detected. Based on the identified intermediates, carboxylic acids and inorganic end-products as well as TOC removal results, a plausible reaction sequence for mineralization of PPN by electrogenerated hydroxyl radicals is proposed.

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## 1. Introduction

Electrochemical Advanced Oxidation Processes (EAOPs) are eco-friendly hydroxyl radical (•OH)-mediated electrochemical treatments in which organic pollutants are non-selectively destroyed by *in-situ* electrochemically generated hydroxyl radical (•OH). These radicals are formed either at the anode surface from water discharge reaction (Eq. (1)) [1–4], or in the bulk of the solution *via* Fenton's reaction (Eq. (2)) between externally added

catalyst (Fe<sup>2+</sup>) and *in situ* electrogenerated H<sub>2</sub>O<sub>2</sub> [5–9].



In the absence of ferrous iron in the solution, the process is called anodic oxidation (AO). This process is effective with high O<sub>2</sub> evolution overpotential anodes (M) such as PbO<sub>2</sub> or BDD. When using cathodes such as carbon-felt that promotes generation of H<sub>2</sub>O<sub>2</sub>, it is named AO-H<sub>2</sub>O<sub>2</sub> which has been proven to be more efficient compared to corresponding AO due to the generation of weak oxidants such as H<sub>2</sub>O<sub>2</sub> and HO<sub>2</sub>• [10–12].

In electro-Fenton (EF) process, homogeneous •OH are generated from electrochemically assisted Fenton's reaction (Eq. (2)). The

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Fenton's reagent (i.e.  $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ ) is continuously electro-generated/regenerated in the solution by 2-electron reduction of dissolved oxygen (Eq. (3)) and 1-electron reduction of  $\text{Fe}^{3+}$  (Eq. (4)) formed by Fenton's reaction, respectively, at the cathode [13–15]. As such only small quantity of  $\text{Fe}^{2+}$  is required to catalyze the Fenton's reaction.



Hydroxyl radical is the second strongest oxidant after fluorine with very high standard redox potential ( $E^\circ_{\text{OH}/\text{H}_2\text{O}} = 2.80 \text{ V/SHE}$ ) [16]. Therefore  $\bullet\text{OH}/\text{M}(\bullet\text{OH})$  are able to oxidize organics efficiently, till complete mineralization (i.e. transformation to  $\text{CO}_2$ ) [6,17].

EF process is considered more efficient compared to AO because oxidation of organics may occur at the anode surface in addition to the homogeneously generated  $\bullet\text{OH}$  in bulk, depending on the nature of anode material used [18–20]. In fact, when a high  $\text{O}_2$  over potential anode such as BDD, doped  $\text{SnO}_2$  or  $\beta\text{-PbO}_2$  is used, heterogeneous hydroxyl radicals ( $\text{M}(\bullet\text{OH})$ ) are formed at the surface of anode, which have been found to be more effective in mineralization of Fe-carboxylic complexes formed during the EF process, which are highly resistant to oxidation by homogeneous  $\bullet\text{OH}$  in the bulk [6,21]. On the other hand, the use of "active anode" materials such as DSA, noble metals (Pt) and carbon based anodes, usually results in partial mineralization of organic pollutants due to the limited generation of  $\text{M}(\bullet\text{OH})$  at these anode surface [20,22]. However, BDD is highly expensive compared to DSA and carbon based anodes, while the use of  $\beta\text{-PbO}_2$  poses high risk of lead contamination via chemical leaching and Ti/ $\text{SnO}_2$  based electrodes has relatively short service life, even when doped with antimony or cerium [2,23].

Sub-stoichiometric titanium oxides ceramic electrodes, developed in late 80's, could represent a cost effective and efficient alternative anode materials for electrochemical wastewater treatment applications due to their promising characteristic and inexpensive production route [24]. In fact, these electrodes are relatively robust in aggressive media, exhibit high electrical conductivity at room temperature and excellent stability with respect to water oxidation and reduction under anodic ( $>2 \text{ V vs SCE}$ ) and cathodic ( $\sim -1.4 \text{ V vs SCE}$ ), respectively, especially  $\text{Ti}_4\text{O}_7$  [25,26]. They are solely prepared from  $\text{TiO}_2$ , one of the most abundant feed-stocks available on planet, thus they are less expensive materials compared to BDD, Pt or DSA [24,27].  $\text{Ti}_4\text{O}_7$  electrode is a "non-active" electrode like BDD which generates  $\text{M}(\bullet\text{OH})$  via water oxidation (Eq. (1)) [28,29]. Therefore, the mineralization of refractory carboxylic acid complex by  $\text{Ti}_4\text{O}_7(\bullet\text{OH})$  is possible when this electrode is used in EF process. Few studies have reported the potential of this material as electrode in electrooxidation of organic pollutants [27,30–32], but it has not been tested in EF process. This is understandable because EF process is carried out at acidic pH ( $\text{pH} \sim 3$ ) which can be detrimental to the stability of this material. More so, the formation of yellowish  $\text{Ti}(\text{H}_2\text{O}_2)_4$  complex is paramount at this pH due to partial dissolution of titanium oxides, with titanium reacts with  $\text{H}_2\text{O}_2$  and thus inhibiting the Fenton's reaction (Eq. (2)). However, our previous study [33] have shown that plasma deposited  $\text{Ti}_4\text{O}_7$  is highly stable and does not form complex with  $\text{H}_2\text{O}_2$  at circum-neutral pH (5.8) when tested in anodic oxidation with *in-situ*  $\text{H}_2\text{O}_2$  generation (i.e.  $\text{AO-H}_2\text{O}_2$ ) because of high adhesion of the thin coated on the Ti substrate. The high temperature of the "plasma plume" (10 000–15 000 °C) via which  $\text{Ti}_4\text{O}_7$  was deposited ensures

deep fusion/penetration into substrate surface and enhance its sealing and stability.

Propranolol (PPN), is one of the common beta adrenergic antagonists (beta-blockers) pharmaceutical used in treatment of cardiac arrhythmias, hypertension, anxiety therapies, angina, as well as in veterinary medicine; and sometimes used illegally as doping agent in many sports [34,35]. It is also among of most frequently detected beta-blockers in aquatic environment [36]. The major source of PPN in wastewater includes private household, pharmaceutical plant wastewater, livestock impoundments as well as effluents from hospitals and retirement homes [37,38]. Natural remediation paths such as sorption, biodegradation, hydrolysis and photodegradation may attenuate the concentration of PPN in aquatic environment, but studies have shown that it has high degree of persistence and bioaccumulation in water bodies [39,40]. Ecotoxicology studies indicate that aquatic organisms show high sensitivity to PPN [41]. It can affect cardiac rhythm, generate abnormalities or causes reproductive impairment in fish, Japanese medaka (*Oryzias latipes*) and had specific toxicity towards plankton and green algae [42–44]. Additionally, there are several evidences on the additive effects of PPN, which means that even at low concentration, it might contribute to the global toxic potential of the total compounds in the aquatic environment [42].

Advanced oxidation processes (AOPs) such as ozonation or ozone/ $\text{Fe}^{2+}$  [45,46], pulse and  $\gamma$  radiolysis [47], ferrate (VI) oxidation [48], solar or UV photolysis [49] and solar or UV  $\text{TiO}_2$  photocatalysis [50,51] have been reported to achieve good degradation but relatively poor mineralization of PPN in aqueous solution. On the other hand, better mineralization of PPN was obtained with EAOPs treatments [17,52].

In this study, we investigated for the first time the potential of  $\text{Ti}_4\text{O}_7$  as a suitable anode in EF degradation of aqueous solutions of PPN using carbon-felt cathode. The effect of applied current and initial concentration on the degradation rate and mineralization of PPN solution were carefully studied. Comparative studies under anodic oxidation and EF using  $\text{Ti}_4\text{O}_7$  and DSA anodes were investigated on both degradation of PPN and mineralization of its aqueous solution. Aromatic intermediates, short-chain carboxylic acids as well as inorganic ions formed during the treatment were detected and quantified by chromatographic techniques and based on these intermediates and end-products, a plausible mineralization pathway was proposed.

## 2. Experimental

### 2.1. Chemicals

Analytical grade ( $>99\%$  purity) propranolol hydrochloride,  $\text{C}_{16}\text{H}_{21}\text{NO}_2$ , was purchased from Aldrich and used without further purification. Para-hydroxybenzoic acid (pHBA) (99.5%), anhydrous sodium sulfate (99%), potassium sulfate (99%) and Iron II sulfate heptahydrate (99.5%) were supplied by Aldrich, Acros organics and Chimie-Plus. Methanol (HPLC grade, Aldrich), sulfuric (98%, Acros organics), phosphoric (85%, Aldrich) and acetic acids (glacial p.a., Acros organic) were obtained as reagent grade. Ammonium oxalate (99%) and sodium nitrate (99.5%) were obtained from Merck and Aldrich. Oxalic, oxamic, glyoxylic, and maleic acids were analytic grade supplied by Acros organics, Fluka and Alfa Aesar. All solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q system with resistivity  $>18 \text{ M}\Omega \text{ cm}$  at 25 °C.

### 2.2. Instruments and analytical procedures

The solution pH was measured with a CyberScan pH 1500 pH-meter from Eutech Instruments. Electrolyses were performed with a Hameg HM7042-5 triple power supply at constant current. The

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