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Research Paper

Sub-stoichiometric titanium oxide as a new anode material for electro-Fenton process: Application to electrocatalytic destruction of antibiotic amoxicillin

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ABSTRACT

This study report, for the first time, the potential use of sub-stoichiometric titanium oxide (Ti_4O_7) elaborated by plasma deposition, as an efficient, stable and cost-effective anode material for electrocatalytic oxidation of organic pollutants by electro-Fenton process. The antibiotic amoxicillin (AMX) was selected as target pollutant and the oxidative degradation of this drug was ensured by hydroxyl radicals generated both at Ti_4O_7 surface by oxidation of water and in the bulk solution from electrocatalytically produced Fenton's reagent. A quick oxidation of 0.1 mM (36.5 mg L^{---1}) AMX was obtained in a short electrolysis time for all applied current studied while its almost complete mineralization was attained even at a low current intensity of 120 mA. The performance of this new anode material in term of degradation kinetics, mineralization current efficiency (MCE) and energy cost was compared with boron doped diamond (BDD) and other conventional anodes such as platinum (Pt) and dimensional stable anode (DSA). Results showed that Ti_4O_7 provides similar oxidation rate and MCE as BDD at all current studies, while it give significantly better results than DSA and Pt anodes. The solutions treated by electro-Fenton process using Ti_4O_7 anode showed low percentage bioluminescence inhibition to *V. fischeri* bacteria, indicating excellent detoxification of the AMX solution. Therefore, Ti_4O_7 anode appears to be an interesting cost-effective alternative anode material to BDD and other industrial electrodes for electro-Fenton processes since its production is very inexpensive when compared to BDD.

1. Introduction

Electro-Fenton (EF) oxidation is one of the most prominent and efficient advanced oxidation processes (AOPs) that have been widely studied for the removal of toxic/persistent organic pollutants (POPs). It involves the formation of hydroxyl radicals (•OH) in the bulk via Fenton's reaction (Eq. (2)) between continuously electrogenerated H_2O_2 at a suitable cathode (Eq. (1)) fed with air/O_2 and iron catalyst initially added to the treated solution at catalytic quantities [1–6]. Interestingly the catalyst (Fe^{2+}) consumed in reaction (2) is electrocatalytically regenerated in reaction (3).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

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

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

Although the oxidation of the pollutants in EF process occurs primarily in the bulk, thanks to the large amount of homogeneously generated hydroxyl radicals (•OH) via electrocatalytically generated Fenton's reagent, the nature of the anode material (M) plays also a significant role on the process efficiency due to the generation of heterogeneous hydroxyl radical M(•OH) (Eq. (4)) which contributes to the overall oxidation/mineralization of the organic pollutants. This is particularly the case of non-active anodes such as BDD or PbO_2 with large O_2 evolution overvoltage [7–13]. Several studies have shown that M(•OH) is more efficient in oxidation of highly recalcitrant short-chain carboxylic acids, which are the ultimate intermediate products before complete mineralization of organics by AOPs, whereas •OH produced in the bulk is relatively less reactive toward this species [[14–18]]. Therefore, the nature of anode material is an important parameter in EF process for an efficient treatment of persistent/toxic organic pollutants.

$$M + H_2O \rightarrow M({}^{\bullet}OH) + H^+ + e^- \quad (4)$$

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Many authors have reported partial mineralization of organics by EF process when "active" anodes like Pt and DSA, that have lower O_2 evolution overpotential, are utilized as anode materials due to the chemisorption of the generated M(•OH) on anode surface making them less efficient in mineralization of recalcitrant organics [8,19–23]. In contrast, almost complete mineralization has been achieved in EF oxidation of persistent organics with non-active anode like BDD [3,24–28] for which M(•OH) is more available due to its physisorption. All these reports pointed out that the efficiency of EF process can be significantly enhanced by using a non-active anode such as BDD. However, BDD anode is highly expensive and currently not economically viable on industrial scale [11,29]. Other available non-active anodes such as doped PbO_2 and SnO_2 have never been utilized in EF process due to their stability and the likely leaching of toxic ions to treated solution.

Magnéli phase ceramic electrodes based on sub-stoichiometric titanium oxides with generic formula Ti_nO_{2n-1} $(3 \leq n \leq 9)$ were developed in early '80s, but recently investigated as low cost alternative electrode materials in electrochemical water treatment because they are produced from TiO_2, one of the most abundant feedstocks available on the planet [30–32]. Several oxides in this series, especially Ti_4O_7 exhibits high electrical conductivity at room temperature, good corrosion resistant and high chemical stability even in extremely corrosive media [33–36]. Generally Ti_4O_7 can be prepared by annealing Ti film in oxygen environment [32] or reducing TiO_2 by using carbon [33], H_2 [37], NH_3 [38], N_2 [39], Zr [40], and spark plasma sintering [41]. Studies have shown that this electrode behaves as non-active anode, i.e., generates weekly sorbed •OH on its surface, that can lead to the electrochemical combustion of organics to CO_2 [32,42,43]. Some authors, including our group, have studied the potential of this anode material at low currents in anodic oxidation of organic pollutants [44–46], but no study available in literature on application of this anode material in EF process.

In this context we investigated for the first time, the use of Ti_4O_7 as a suitable anode material for EF process. Ti_4O_7 films can be manufactured by plasma coating, which is a widely spread technology, largely used for many types of applications (corrosion protection, abrasion resistance, thermal barriers, etc.). It was prepared by two step technique: (i) reduction of TiO_2 with coke to produce Ti_xO_{2x-1} powder and (ii) plasma elaboration of Ti_xO_{2x-1} on Ti-alloy substrate at 10 000–15 000 °C accompanied by conversion of all sub-oxides of Ti to Ti_4O_7 [46]. Plasma coating technology makes it possible to coat large surfaces, up to 1 m^2 or even larger, which is a definite advantage and cost-reducing technique for commercial production of electrodes compared to the chemical vapor deposition technology used in fabrication of BDD anodes. Therefore we investigated the ability of this anode for oxidation of a common antibiotic, amoxicillin (AMX), which was used as target pollutant and to the mineralization of its aqueous solution. Comparative experiments were carried out with anode materials such as BDD, Pt and DSA under same operating conditions. Moreover, the energy consumption of EF process related to each anode material as well as evolution of the acute toxicity during the treatment were assessed.

2. Materials and methods

2.1. Chemicals

AMX ($C_{16}H_{19}N_3O_5S$), sodium sulfate (Na_2SO_4), iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) were obtained from Sigma-Aldrich. Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) used to adjust solution pH were of analytical grade from Acros Organics and Fluka. Oxalic ($H_2C_2O_4$), oxamic ($C_2H_3NO_3$), acetic ($C_2H_4O_2$), maleic ($C_4H_4O_4$), glycoxylic ($C_2H_2O_3$) and malonic ($C_3H_4O_4$) acids used as standards for quantifying short-chain aliphatic carboxylic acids generated during EF treatment were obtained from Acros, Fluka and Alfa Aesar. Bioluminescent bacteria *Vibrio fischeri* and the activation reagent LCK 487 LUMISTOX were supplied by Hach Lange France SAS. Organic solvents and other chemicals used were either HPLC or analytic grade from Sigma-Aldrich, Fluka and Merck. All solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q system with resistivity>18 MΩ cm at 25 °C.

2.2. Electrochemical cell

The electrolyses were performed in a 250 mL undivided cylindrical glass cell equipped with two electrodes and stirred with PTFE magnetic bar. The anode was an electrode of 24 cm^2 surface area (4 cm × 6 cm) made of either Ti_4O_7 thin film plasma deposited on Ti alloy, Saint Gobain C.R.E.E., France), commercial pure Pt mesh, commercial DSA (RuO_2–IrO_2 thin film deposited on Ti, Baoji Xinyu GuangJiDian Limited Liability Company, China) or BDD (thin film deposited on Nb support, Condias Gmbh, Germany), while the cathode was a tri-dimensional, large surface area (14 cm × 5 cm × 0.5 cm) carbon-felt (CF) (MERSEN, France). The anode was always centered in the electrochemical cell, surrounded by the CF cathode. Compressed air was continuously bubbled into the cell at about 1 L min^{-1} to ensure an O_2 saturated solution. 230 mL aqueous solutions of 0.1 mM AMX (19.6 mg L^{-1} TOC) containing 0.05 M Na_2SO_4 as supporting electrolyte and 0.1 mM Fe^{2+} (catalyst) were used to conduct the electrochemical experiments at pH 3 and applied current in the range of 10–120 mA. All trials for kinetics measurements and TOC decay of solutions were conducted at room temperature (23 ± 2 °C) and made in triplicate. The average values with an error <2% are reported on the figures.

2.3. Analytical procedures

Electrolyses were performed with a Hameg HM7042-5 triple power supply at constant current. The total organic carbon (TOC) removal was monitored by Shimadzu VCSH TOC analyzer using the non-purgeable organic carbon method with ± 2% accuracy. The data obtained were used to estimate the mineralization degree of treated AMX solution and the mineralization current efficiency (MCE) (using Eq. (5)) for each treated solution at a given electrolysis time based on complete electrochemical oxidation of AMX (Eq. (6)) [14,47].

$$\mathrm{MCE}\,(100\%) = \frac{nFV_s\Delta(TOC)_{exp}}{4.32x10^7 mIt} \times 100 \quad (5)$$

where F is the Faraday constant (96487C mol^{-1}), V_s is the solution volume (L), 4.32×10^7 is a conversion factor (=3600 s h^{-1} × 12,000 mg of C mol^{-1}), m is the number of carbon atoms of AMX (16C atoms), I is the applied current (A) and n is the number of electron consumed per molecule of AMX; taken to be 94 assuming complete mineralization of AMX into CO_2, NO_3^- and SO_4^{2-} according to Eq. (6).

$$C_{16}H_{19}N_3O_5S + 40H_2O \rightarrow 16CO_2 + 3NO_3^- + SO_4^{2-} + 99H^+ + 94e^- \quad (6)$$

The decay of concentration of AMX was followed by uHPLC (Thermo Scientific) model "Ultimate 3000" equipped with a DAD detector and a RP-18 Hypersil 1.9 μm (10 cm × 2.1 mm) column eluted with water/methanol/acetic acid 92:6:2 at flow rate of 0.2 mL min^{-1}. Short-chain carboxylic acids generated during the EF treatment were identified and quantified by ion-exclusion HPLC using Merck Lachrom liquid chromatograph equipped with a L-2130 pump fitted with a C18 Acclaim OA, 4 mm × 25 cm (i.d.) column at 40 °C, and coupled with a L-2400 UV detector selected at wavelength of 210 nm, using 1% H_2SO_4 at 0.2 mL min^{-1} as mobile phase. NH_4^+, NO_3^- and SO_4^{2-} ions released into electrolyzed