Electrochemical degradation of amoxicillin in acidic aqueous medium using TiO\textsubscript{2}-based electrodes modified by oxides of transition metals

Jaxiry Shamara Barroso Martínez\textsuperscript{1} • Antonia Sandoval González\textsuperscript{1} • Mónica Cerro López\textsuperscript{2} • Fabricio Espejel Ayala\textsuperscript{1} • Jesús Cárdenas Mijangos\textsuperscript{1} • José de Jesús Treviño Reséndez\textsuperscript{1} • Yunny Meas Vöng\textsuperscript{1} • Juan Manríquez Rocha\textsuperscript{1} • Erika Bustos Bustos\textsuperscript{1}

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Abstract

One of the most widely used antibiotics is amoxicillin (AMX), which is the most widely used in humans and animals, but it is discharged metabolically due to its indigestibility. Conventional biological and physicochemical methods for removing AMX from water are not enough to mineralize it; it is only concentrated and transferred to produce new residues that require further processing to remove the new residues. In this research, naked and modified surfaces with TiO\textsubscript{2} nanotubes (TiO\textsubscript{2},nt) electrophoretically modified with PbO\textsubscript{2}, IrO\textsubscript{2}, RuO\textsubscript{2}, and Ta\textsubscript{2}O\textsubscript{5} were used to evaluate their efficiency in the electrochemical degradation of AMX in acid media (0.1 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4}). After their comparison, Pb-Ta 50:50|TiO\textsubscript{2},nt|Ti showed the highest removal efficiency of AMX (44.71%) with the lowest specific energy consumption (8.69 ± 0.78 kWh Kg COD\textsuperscript{-1}) and the average instant current efficiency of 26.67 ± 9.19%, in comparison with the others naked and modified surfaces of TiO\textsubscript{2},nt|Ti.

Keywords Amoxicillin • TiO\textsubscript{2} nanotubes • Electrophoretic modification • Transition metal • Emerging organic compound

Introduction

Due to the increase in the world’s population, it is predicted that in the coming years, the demand for healthy water will increase by 55% (Gopinath et al. 2020; Suhaimy et al. 2020). Although industries treat their wastewater with conventional processes, these are not efficient in degrading all pollutants, especially emerging organic compounds (EOCs) (De la Cruz et al. 2013). EOCs are those organic pollutants that have not been recognized by existing environmental legislation, but it has been shown that these pollutants are affecting aquatic ecosystems and their environment (Bueno et al. 2012; Giwa et al. 2021; Majumder et al. 2019; Phoon et al. 2020; Rasheed et al. 2019). In the case of antibiotics, studies by Klein et al. (2018) found that from 2000 to 2015, their consumption increased by 65% and that some of these antibiotics are only partially metabolized allowing a fraction of them to be excreted from the body in an unchanged form after consumption (Rasheed et al. 2019; Ye et al. 2019). The mode of use, types, and concentrations of antibiotics are not the same for all countries; there are concentrations from ppm to ppt, even after the wastewater has been treated (Wen et al. 2014); other studies show that antibiotics are present in different ecosystems (Wang and Zhuan 2020), although in low concentration, but they remain biologically active, causing long-term resistance of bacteria, generating a negative impact on human and animal health (Hou et al. 2019; Phoon et al. 2020).

One of the most widely used antibiotics is amoxicillin (AMX, C\textsubscript{16}H\textsubscript{19}N\textsubscript{3}O\textsubscript{5}S) (PubChem 2021; Wang and Wang 2016). In traditional biological wastewater treatment, AMX exhibits stable chemical properties, biological toxicity, and a
low rate of biodegradation (Song et al. 2016). Conventional methods for removing antibiotics from water include coagulation (Bratby 2016), ozone (O3) and O3-H2O2 (Bavasso et al. 2020) biological systems as activated sludge, membrane, and sequential bioreactor (Wang et al. 2020), inverse osmosis (Baheri et al. 2016), and adsorption by activated carbon (Perrich 2018); the disadvantage being that these contaminants are not only mineralized, but only concentrated and transferred to produce new residues that require further processing to remove the new residues. In some works, amoxicillin mineralization has been reported by different methods: using TiO2-activated carbon composites, 50 to 100% of 50 mg L\(^{-1}\) of amoxicillin at pH 3 to 10 was removed with sunlight for 180 min (PubCHem 2021). Using TiO2 nanotubes with graphite and adding KBrO\(_3\), a degradation of almost 100% is achieved (Gar et al. 2016). With hybrid processes, ultrafiltration membrane, activated carbon adsorption, and ultrasound irradiation in 10 ppm of amoxicillin, 99.5% were removed (Secondes et al. 2014), and with adsorption, membrane, and ultrasound irradiation for 0.1 mg L\(^{-1}\), 99% was removed (Naddeo et al. 2020).

Advanced oxidation processes (AOPs) with modified electrodes are other promise technology, which shows high removal percentages of pharmaceutical compounds as paracetamol (Brillas et al. 2005), metoprolol (Dirany et al. 2012), sulfachloropiridazine (Cavalcanti 2013), omeprazole (García-Segura et al. 2014), chloramphenicol (Olvera-Vargas et al. 2014), ranitidine (Salazar 2014), phantetra (Panizza et al. 2014), and amoxicillin (León et al. 2020). The oxidant power of AOPs is determined by the high oxidation overpotential to O2 evolution and the sorption enthalpy of electrogenerated hydroxyl radicals (Marcelino et al. 2017; Sopaj et al. 2015; Tan et al. 2020; Zha et al. 2014). AOPs are used because of their rapid reaction rate and strong oxidation capacity, which are effective for antibiotic degradation in aquatic environments (Benjedim et al. 2020; Moura et al. 2018; Seo and Park 2009; Wang and Zhuan 2020). In AOPs, the dimensional stable anodes (DSA®) are used, which are constructed by a thin film of transition metal oxides over metal as titanium (Ti) by its low cost; the Ti is sandblasted to increase the exposed area to include the metallic oxides, as it has been reported previously (Herrada et al. 2016, 2018, 2020; León et al. 2020).

In the case of nanostructured TiO2, it is used because it has a relatively high quantum value, easy accessibility, low toxicity, high physical/chemical stability, large surface area, fast degradation rates, is non-toxic, is biocompatible with the environment, and can be easily synthesized (Gopinath et al. 2020; Molina-Reyes et al. 2020). TiO2 nanotubes can be obtained by different synthesis methods, (a) hydrothermal (Subramaniam et al. 2020), anodization (Diao et al. 2020; Suhaimy et al. 2020), microwave (Martínez-Sánchez et al. 2019), impregnation (Kulkarni et al. 2016), sol-gel (Muswareen et al. 2019), solvothermal (Oh et al. 2019), template synthesis, and chemical reduction (Peng et al. 2021). Anodization is considered the most convenient and effective method for preparing high-quality TiO2 nanotubes due to its good controllability, simple operation, low cost, and environmental friendliness (Liu et al. 2013). Currently, there are several researches focused on modifying TiO2 nanotubes with different materials, for example, TiO2-Ru (Gopinath et al. 2020), Co/Bi/TiO2 NTA (Ahmadi and Wu 2020), TiO2-S (Yang et al. 2021), Co-TNT (Caia et al. 2020), TiO2 NTA/CuO (Koiki et al. 2020), Fe-TNT (Subramaniam et al. 2020), TNT/Fe2O3/TiO2 (Chen et al. 2018), TNTs@GO (Lei et al. 2018), TiO2/SiO2 (Rasheed et al. 2019), g-C3N4/Ti3C2/TiO2 (Diao et al. 2020), TiO2/NTs/AgBr/BrOBr (Ye et al. 2018), Ag/NTA (Peng et al. 2021), CeO2 (Koiki et al. 2020), doped Zn (Xu et al. 2005), N2 (Lin et al. 2011), SnO2 (Tsai et al. 2017), CdS (Zhang et al. 2018), CdSe (Zhang et al. 2009), PbS (Zhang et al. 2016), and Pt (Zhou et al. 2018). Most of these nanomaterials have been used for the degradation of dyes or other organic compounds; these TiO2-doped nanotubes have not been proposed to degrade amoxicillin.

In this research, naked and modified surfaces with TiO2 nanotubes (TiO2-nt) electrophoretically modified with PbO2, IrO2, RuO2, and Ta2O5 were used to evaluate their efficiency in the electrochemical degradation of AMX in aqueous media, which is an example of the EOCs, and it has not been reported before. This pharmaceutical product has been electrooxidized using IrO2-Ta2O5/Ti and RuO2-Ta2O5/Ti in acidic solutions (0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\)) and neutral solutions (0.1 mol L\(^{-1}\) Na2SO4) in a previous study (Sopaj et al. 2015). On this occasion, the TiO2-nt modified with IrO2-Ta2O5, RuO2-Ta2O5, and PbO2-Ta2O5 are considered to electrooxidize AMX in acidic media (0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\)).

**Experimental section**

**Preparation of modified electrodes**

Titanium alloy grade 2 (ASTM B265) was used in this study by its excellent balance of strength, ductility, toughness, and weldable; this material shows corrosion resistance in highly oxidizing and mildly reducing environments (ITA 2005). Ti plates were modified to morphological characterization 3.0 cm in height, 1.0 cm in width, and 0.1 cm in thickness (Fig. 1a). Ti cylinders were also modified to AMX electrooxidation; they were 0.7 cm in diameter and 5.0 cm in height (Fig. 1b).

The Ti plates and cylinders were anodized to form TiO2 nanotubes (TiO2-nt) by a voltage application of 30 V for 1, 2, 3, and 4 h (Cerro-López et al. 2014) and then modified with the different oxide deposits and their combinations. The growth of TiO2 nanotubes is carried out by (a) the formation...
of the barrier layer, (b) the oxidation of titanium, and (c) the dissolution of Ti, which is related to the concentration of F- ions. At the beginning of the anodization, 0.5 mA is recorded; after 2 min, this current drops to 0.3 mA, and after 5 min, 0.1 mA is obtained. The current drop is attributed to the oxidation of Ti to form TiO₂. The current increases slightly with time but has fluctuations due to the competition between the growth of the titanium oxide tubes and the dissolution of the oxide for the formation of stable tubes (Sreekantan et al. 2009; Sun et al. 2009; Zhao et al. 2005).

These deposits were IrO₂–Ta₂O₅ (Ir-Ta), RuO₂–Ta₂O₅ (Ru-Ta), and PbO₂–Ta₂O₅ (Pb-Ta) with the combinations 100:0, 70:30, 50:50, 30:70, and 0:100. In these experiments, a DC-power supply model GP-4303DU was used with a constant stirring rate of 300 rpm considering the TiO₂,nt over Ti as working electrode and a Ti plate or mesh as counter-electrode for the Ti plate and cylinder, respectively, considering 1 cm of separation between working and counter-electrode (Fig. 1).

To get the TiO₂,nt, a mechanical pre-treatment of the Ti surfaces was made with the polishing paper of 120, 240, 360, 1500, and 2000 particles, 2 inches in presence of water, and finally with alumina (Al₂O₃) of 0.3 mm of diameter with a polishing cloth. All these modified surfaces were cleaned by ultrasound in acetone, ethanol, and deionized water for 10 min in each solvent. In all cases, the modified electrodes were rinsed with deionized water and dried with nitrogen.

To modify the TiO₂,nt by electrophoretic anodization with PbO₂ and Ta₂O₅ in a relation w/v of 100:0, 30:70, 50:50, and 70:30, the precursor solutions used were 0.5 mol L⁻¹ Pb(NO₃)₂ (Meyer, 99%) in 0.1 mol L⁻¹ HNO₃ (J. T. Baker, 70%) and 1.0 mol L⁻¹ TaCl₅ (Strem Chemicals, 99.9%) in isopropanol (Karal, 99.5%) (Herrada et al. 2016, 2018, 2020; Trasatti and Petrii 1991) applying a current density of 50 mA cm⁻² by 5 s (León et al. 2020) in a two-electrode electrochemical cell, where the Ti plate or cylinder was the working electrode with a Ti plate or mesh as counter-electrode, respectively (Fig. 1).

To modify the TiO₂,nt by electrophoretic anodization of Ir, Ru, and Ta, a current density of 20 mA cm⁻² by 20 min with constant stirring (300 rpm) was used; the precursors’ solutions used were 0.1 mol L⁻¹ H₂IrCl₆ (Stream Chemicals, 99.9%) in 50% HCl (J. T. Baker, 38%) and isopropanol (Karal, 99.5%) in a relation 2:1; in the case of Ru deposition, 0.1 mol L⁻¹ RuCl₃ •H₂O (Strem Chemicals, 99.9%) in 50% HCl and isopropanol 2:1, and 1 mol L⁻¹ TaCl₅ (Strem Chemicals, 99.9%) in isopropanol under vigorous stirring.

The Ru-Ta and Ir-Ta ratios employed in the precursors’ solutions were 100:0, 30:70, 50:50, and 100:0 w/w in a two-electrode electrochemical cell, where the Ti plate or cylinder was the working electrode with a Ti plate or mesh as counter-electrode, respectively (Fig. 1), which were used in the electrodeposition as it has been reported before (Herrada et al. 2018, 2020; León et al. 2020). After electrophoretic deposition of Ru-Ta and Ir-Ta with the different ratios, the synthesis of metal oxides was obtained in two-step thermal decomposition, 523 K for 10 min and 723 K for 1 h (Herrada et al. 2018, 2020; León et al. 2020).

During this study, before using the different modified electrodes in the different activities of morphological characterization and AMX electrooxidation, they were polarized with a constant current of 10 mA by 5 min in 0.5 mol L⁻¹ H₂SO₄ (J. T. Baker, 95.9%) with a constant stirring (500 rpm).

**Characterization of naked and modified electrodes**

The electrochemical characterization was performed to define the superficial surface area of the different naked and modified electrodes using a three electrodes cell with 0.1 mol L⁻¹ H₂SO₄ (J. T. Baker, 98%) as support electrolyte at 298 K, with Pt wire (BASi), Ag | AgCl 3M NaCl (BASi), and naked
and modified Ti, as counter, reference, and the working electrode, respectively, using a BASi-Epsilon® potentiostat from Bioanalytical Systems Inc. In all these measures, the electrochemical cell was saturated with ultra-pure nitrogen (Praxair, grade 5.0) for 10 min to eliminate the oxygen. With this experimental set, the electroactive area \((A_e)\) of the naked and modified cylindrical electrodes was calculated with the capacitance method, using the capacitive current of the double layer \((C_{dl})\) generated in presence of 0.1 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\) between \(\pm 10\ \text{mV}\) around the equilibrium potential, in one cycle at 20, 40, 60, 80, and 100 mV s\(^{-1}\) (Gülfen et al. 2020; Herrada et al. 2018 and 2020; León et al. 2020; Ren et al. 2015), and roughness factor \((\text{R})\) was calculated by each electrode in the study by the division of geometric area \((A_g)\) between electroactive area \((A_e)\), as \(R = A_g/A_e\) (Herrada et al. 2018, 2020; León et al. 2020; Ren et al. 2015). All these results were evaluated by quadruplicate to \(\text{TiO}_2\)-nt.

The morphology of naked and modified electrodes was characterized by scanning electron microscopy coupled to energy-dispersive X-ray spectroscopy (SEM-EDX) using a Jeol JSM-6500LV equipment with 15 eV and EDS Bruker XFlash6110 as the detector. EDS analysis was achieved in the center of each electrode taking in images at 2500×, considering an area of a circle of 1.3 \(\mu\)m of radius and a depth of 1.2 \(\mu\)m.

**Electrochemical degradation of amoxicillin using modified electrodes**

The AMX electrochemical oxidations were performed using a Ti cylinder naked and modified with Pb, Ir, Ru, and Ta to have Pb-Ta 30:70, Pb-Ta 70:30, Ru-Ta 30:70, Ru-Ta 70:30, Ir-Ta 30:70, and Ir-Ta 70:30 as anodes, with a Ti mesh cathode around it (León et al. 2020). With the same configuration of the electrochemical cell and the different naked and modified electrodes, the corresponding hydrodynamic curves were made using 0.1 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\) in the presence of 10 mg L\(^{-1}\) AMX (Across Organics) at 300 rpm using a two-electrode cell arrangement in the presence of Ti mesh and the naked and modified Ti cylinders as the counter and the working electrode, respectively.

For the construction of the hydrodynamic curves, from the cyclic voltammetry, were selected ten potentials from equilibrium potential to obtain different chronoamperometries with a constant potential of 0.01, 0.34, 0.67, 1.00, 1.34, 1.67, 2.00, 2.34, 2.67, and 3.00 V vs. Ag | AgCl 3M NaCl to get the final current density after 5 min of each electrolysis and construct the hydrodynamic curves with current density vs. constant potential by duplicate.

After the construction of the different hydrodynamic curves, the working current density for the AMX electrochemical degradation in 0.1 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\) was selected. To the electrolysis of AMX, a potentiostat–galvanostat Epsilon BASi was used applying 100 \(\mu\)A cm\(^{-2}\) with 300 rpm, and the AMX electrochemical degradation was measured by UV-Vis spectrophotometry (Fig. 2a) with a PerkinElmer Lambda XLS equipment obtaining the calibration curve with the different spectra of samples (Fig. 2b), where the UV absorption characteristic of AMX is at 235 nm by the electronic transition \(\pi\rightarrow\pi^*\) of the aromatic ring of AMX (Gülfen et al. 2020) in 0.1 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\) and the representative equation is \(A(\text{a.u.}) = 6 \times 10^{-5}\) (AMX mg L\(^{-1}\))\(^{-1}\) \(1 \times 10^{-4}\) and \(R^2 = 0.9956\). With this calibration curve, the removal efficiency of AMX \((\eta\%)\) was obtained with the initial concentration \((C_0)\) and final concentration \((C_f)\) (as Eq. 1 shows).

\[
\eta\% = \left(\frac{C_0 - C_f}{C_0}\right) \times 100
\]  

(1)

AMX degradation was monitored by chemical oxygen demand (COD) analysis according to Method 8000 using the Reactor Digestion Method defined in the Hach Water Analysis Manual®. A colorimetric determination was carried out with units of mg L\(^{-1}\) of COD, as the number of mg of O\(_2\) consumed per liter of the sample under the procedure conditions, which was programmed on the DR/2010 spectrophotometer. The procedure consisted of heating the sample for 2 h with a potent oxidizing agent (potassium dichromate). The oxidizable organic compounds react, reducing the dichromate ion \((\text{Cr}_2\text{O}_7^{2-})\) to a green chromic ion \((\text{Cr}^{3+})\). Using a concentration from 0 to 150 mg L\(^{-1}\) \(\text{Cr}_2\text{O}_7^{2-}\), the amount of remaining \(\text{Cr}^{3+}\) was determined, and using a concentration from 0 to 150 mg L\(^{-1}\), the amount of \(\text{Cr}^{3+}\) produced was determined.

COD analyses were done in triplicate, with samples extracted during electrolysis to determine AMX degradation after 120 min of electrooxidation to evaluate the removal efficiency of COD using naked Ti and modified \(\text{TiO}_2\)-nt | Ti by Ir, Ru, and Pb without and with Ta in a relation of 100:0, 70:30, 50:50, 70:30, and 100:0. AMX mineralization was monitored from the removal of total organic carbon (TOC), determined on a TOC analyzer Shimadzu apparatus (model TOC-L). The specific energy consumption (EC, kWh m\(^{-3}\)) during electrochemical treatment was calculated according to Eq. 2 (Huang et al. 2017; León et al. 2020; Zavala Salazar 2011):

\[
\text{EC} = \frac{(E_{\text{cell}} \times I_t)}{(1000 \text{ V})}
\]  

(2)

where \(E_{\text{cell}}\) is the average potential difference between the anode and cathode during electrolysis \([\text{V}]\); \(I\) is the current \([\text{A}]\); and \(t\) is the electrolysis time \([\text{h}]\).

The specific energy consumption per unit of mass of COD \((E_{\text{sp}}\) = kWh Kg COD\(^{-1}\)) was calculated from Eq. 3:

\[
E_{\text{sp}} = \frac{(1000 \times E \times I \times t)}{(\text{COD}_{t=0 \text{ min}} - \text{COD}_{t=400 \text{ min}})} \times V_s
\]  

(3)

where \(E\) is the potential \([\text{V}]\); \(I\) is the electric current \([\text{A}]\); \(t\) is the electrolysis time \([\text{h}]\); \(\text{COD}_{t=0 \text{ min}}\) is the COD at the start
of the electrochemical degradation process \(=\) mg L\(^{-1}\); COD\(_{400}\) min is the COD at the end of the electrochemical degradation process (mg L\(^{-1}\)); and \(V_s\) = volumetric volume of the sample \(=\) L.

The instant current efficiency (ICE, \%) was calculated from Eq. 4 considering the effectiveness and feasibility of AMX degradation (Huang et al. 2017; León et al. 2020; Zavala Salazar 2011):

\[
\text{ICE} (%) = \frac{F \cdot V_s \cdot (\Delta \text{COD})}{8000 \cdot I \cdot \Delta t}
\]

where \(F\) is the Faraday constant \(=\) 96,485 C mol\(^{-1}\); \(V_s\) is the volume of the solution \(=\) L; \(\Delta \text{COD}\) is the experimental COD decrease (mg L\(^{-1}\)) in the time interval \(\Delta t\) (h); and \(I\) is the current \(=\) A.

Discussion of results

Morphological characterization of naked and modified electrodes

The naked Ti shows a presence of Ti (69.21\%), O (17.03\%), C (11.24\%), and Si (2.52\%), while the TiO\(_2\)nt shows the different composition of these elements (Table 1) with Ti (close to 30\%), O (close to 70\%), and C (between 2 and 6\%) without the presence of Si because the anodization to construct the nanotubes eliminates the silica over the surface of titanium, with the decrease of carbon when increasing the anodization time by the possible impurity in the same surface at 1 h (1.97\%), 2 h (6.34\%), 3 h (5.05\%), and 4 h (4.92%).

Additionally, the relation of titanium and oxygen in the EDS of TiO\(_2\)nt is 1:2; this result validates the atomic composition of a compacted and disorganized film of TiO\(_2\) showing nanotubular structures with a diameter of 50.10 ± 7.11 nm after 1 h (Fig. 3a), 45.34 ± 7.01 nm after 2 h (Fig. 3b), 47.42 ± 7.31 nm after 3 h (Fig. 3c), and 48.77 ± 7.78 nm after 4 h (Fig. 3d). When increasing the anodization time just to TiO\(_2\)nt 4 h (Fig. 3d), it shows regions without nanotubes, with major dispersion and disorder.

Figure 4 shows the Raman spectra of naked Ti and TiO\(_2\)nt at different anodization times, where there are five signals at shifts of 142, 204, 394, 514, and 632 cm\(^{-1}\), corresponding to the vibrational modes \(E_{1g}, E_{2g}, B_{1g}, A_{1g}, B_{1g}\), and \(E_{3g}\) for anatase crystalline phase, respectively (González et al. 2019). Furthermore, the signals at shifts of 448 and 621 cm\(^{-1}\) were assigned to the vibrational modes \(E_g\) and \(A_{1g}\) for the rutile crystalline phase (Boda and Shah 2017). A comparative revision of SEM (Fig. 3), EDX (Table 1), and Raman spectroscopy (Fig. 4) result revealed that the electrochemical anodizing of Ti foils produced nanotubular structures of TiO\(_2\) having a chemical composition with the predominance of anatase crystalline phase.

The peaks with a Raman shift of 448 cm\(^{-1}\) and 621 cm\(^{-1}\) are characteristic of the rutile phase of TiO\(_2\), which are related to \(E_g, B_g, A_g\) by symmetric stretching, symmetric bending, and asymmetric bending, respectively, by the O-Ti-O bonding (Boda and Shah 2017). From the SEM (Fig. 3), EDX (Table 1), and Raman (Fig. 4) analyses, it is evident that electrochemical anodization leads to the formation of nanotubular structures with a chemical composition in a major proportion of anatase phase and minor presence of rutile phase. Additionally, the increase of anodization time is proportional to the increase of the anatase and rutile signals.

This result indicates that the anodization time is indifferent between 1 and 3 h as Raman shows (Fig. 4) with the same anatase and rutile proportion because at the fourth hour begins the disorganization of the nanotubular structures of TiO\(_2\)nt. By these results, the selected anodization time was
1 h to continue the modification of TiO$_2$,nt with the different concentrations of electrocatalyzers included in this study: Pb, Ir, Ru, and Ta.

**Electrochemical characterization of naked and modified electrodes**

In the characterization of the different modified electrodes by the capacitance method (Trasatti and Petrii 1991) to define the electroactive area (Table 2), the Ru-Ta 50:50 shows the highest electroactive area (13.45 cm$^2$) and roughness (1.93) ≈ Pb (12.97 cm$^2$; 1.86) > Ru-Ta 70:30 (11.98 cm$^2$; 1.72) ≈ Ru-Ta 30:70 (11.54 cm$^2$; 1.65) > Ta (11.15 cm$^2$; 1.60) ≈ Ir-Ta 70:30 (10.88 cm$^2$; 1.56) > Ru (7.81 cm$^2$; 1.12) ≈ Pb-Ta 30:70 (6.58 cm$^2$; 0.94) > Ir-Ta 50:50 (6.25 cm$^2$; 0.90) ≈ Ti (5.00 cm$^2$; 0.72); the other electrodes show less electroactive area than Ti:Ir-Ta 30:70 (4.03 cm$^2$; 0.58) ≈ Pb-Ta 70:30 (3.77 cm$^2$; 0.54) ≈ Pb-Ta 50:50 (3.71 cm$^2$; 0.53) > TiO$_2$,nt (3.12 cm$^2$; 0.45) = Ir (2.56 cm$^2$; 0.37). These results show that TiO$_2$,nt with the different concentration of electrocatalyzers increases the $A_e$ and R.

Cyclic voltammetry was obtained for each naked Ti and modified TiO$_2$,nt with the different concentrations of Pb, Ir, Ru, and Ta in 0.1 mol L$^{-1}$ H$_2$SO$_4$ at 20 mV s$^{-1}$ (Fig. 5), where the TiO$_2$,nt with Pb and Ir showed the biggest potential windows (close to 3.2 V vs. Ag | AgCl 3M NaCl) than with Ru.
In the case of the cyclic voltammetry at 200 mV s$^{-1}$ (Fig. 6), all the electrodes show a potential window close to 3.2 V vs. Ag$\mid$AgCl 3M NaCl, where appeared different oxidation peaks at 0.5 V and 1.4 V vs. Ag$\mid$AgCl 3M NaCl; they are related with the change of the oxidation state of the electrocatalyzers, while the potential window of naked Ti and TiO$_2$,nt reaches up to 1.5 V vs. Ag$\mid$AgCl 3M NaCl, where the naked Ti showed minor O$_2$ evolution than TiO$_2$,nt. The electrocatalyzers Ru and Ir have a similar electrochemical behavior by their physicochemical characteristics as metallic conductivity and crystalline structure of rutile, though Ru has the hexagonal close-packed (h.c.p.) structure, while Ir is a face-centered cubic (f.c.c) structure (Michell and Rand 1978).

In the particular case of TiO$_2$,nt modified with Ir-Ta, the electrochemical process associated is related with the Eqs. 5.
and 6 (Michell and Rand 1978) with a proportional decrease of the current density with the decrease of the Ta concentration: Ir-Ta 30:70 > Ir-Ta 50:50 > Ir-Ta 70:30; in the first redox couple Ir\(^{+2}/\text{Ir}^{+4}\) (Eq. 5) with 0.20, 0.15, and 0.10 mA cm\(^{-2}\) for 0.7 V vs. Ag | AgCl 3M NaCl, and for the second couple Ir\(^+4/\text{Ir}^{+5}\) (Eq. 6) with 0.25, 0.20, and 0.12 mA cm\(^{-2}\) for 1.45 V vs. Ag | AgCl 3M NaCl. These results indicate that Ta is necessary to be present in this kind of electrode to increase the electronic transference as they are modified in this study; despite that Ta does not participate in the redox process (Comninellis and Vercesi 1991), it is only a protonic conductor (León et al. 2020).

\[
\text{Ir}^{+2} \rightarrow \text{Ir}^{+4} + 2e^- \quad (5)
\]

\[
\text{Ir}^{+4} \rightarrow \text{Ir}^{+5} + e^- \quad (6)
\]

In the case of the TiO\(_{2,\text{nt}}\) modified with Ru-Ta, there are two electrochemical processes associated by the electrocatalizer (Audichon et al. 2014); the first redox couple Ru\(^{+3}/\text{Ru}^{+4}\) (Eq. 7) in 0.6 V vs. Ag | AgCl 3M NaCl, with the major current density Ru-Ta 70:30 (0.1 mA cm\(^{-2}\)) than Ru-Ta 50:50 and Ru-Ta 30:70 (0.05 mA cm\(^{-2}\)); the second redox couple Ru\(^{+4}/\text{Ru}^{+6}\) (Eq. 8) in 1.3 V vs. Ag | AgCl 3M NaCl, where the electrode with Ru-Ta 70:30 showed the highest current density (0.15 mA cm\(^{-2}\)) than Ru-Ta 30:70 (0.1 mA cm\(^{-2}\)) and Ru-Ta 50:50 (0.08 mA cm\(^{-2}\)).

\[
\text{Ru}^{+3} \rightarrow \text{Ru}^{+4} + e^- \quad (7)
\]

\[
\text{Ru}^{+4} \rightarrow \text{Ru}^{+6} + 2e^- \quad (8)
\]

For TiO\(_{2,\text{nt}}\) modified with Pb-Ta, there are two characteristic electrochemical processes reported in the literature (Mahalingam et al. 2007), the first one is between 0.5 and 0.6 V vs. Ag | AgCl 3M NaCl by the redox coupled Pb\(^{+2}/\text{Pb}^{+3}\) (Eq. 9) with the same current density in the different concentrations of Pb-Ta (0.2 mA cm\(^{-2}\)); the second one between 1.5 and 1.6 V vs. Ag | AgCl 3M NaCl by the Pb\(^{+3}/\text{Pb}^{+4}\) (Eq. 10). In the last case, Ta is important for the electrocatalyst effect of Pb since Ta is a protonic conductor and is favorable to generate interfacial hydroxyl radicals for the electrocatalysis effect (León et al. 2020). In this case, Pb-Ta 50:50 showed the major current density (0.5 mA cm\(^{-2}\)) followed by Pb-Ta 70:30 (0.48 mA cm\(^{-2}\)); Pb-Ta 30:70 showed the lowest current density (0.35 mA cm\(^{-2}\)).

\[
Pb^{+2} \rightarrow Pb^{+3} + e^- \quad (9)
\]

\[
Pb^{+3} \rightarrow Pb^{+4} + e^- \quad (10)
\]

### Table 2
The capacitive current of the double layer (\(C_{dl}\)), electroactive area (\(A_e\)), and roughness (\(R\)) to different naked Ti and modified TiO\(_{2,\text{nt}}\) with Ir, Ru, and Pb in the presence or not of Ta, considering a geometric area (\(A_g\)) of 6.9822 cm\(^2\).

| Electrodes         | \(C_{dl}\) (F) | \(A_e\) (cm\(^2\)) | \(R \quad (A_e/A_g)\) |
|--------------------|----------------|---------------------|------------------------|
| IrO\(_2/\text{Ta}_2\text{O}_5/\text{TiO}_2,\text{nt} | Ti             |                     |                        |
| Ir-Ta 100:0        | 0.0002         | 2.56                | 0.37                   |
| Ir-Ta 70:30        | 0.0007         | 10.88               | 1.56                   |
| Ir-Ta 50:50        | 0.0004         | 6.25                | 0.90                   |
| Ir-Ta 30:70        | 0.0002         | 4.03                | 0.58                   |
| RuO\(_2/\text{Ta}_2\text{O}_5/\text{TiO}_2,\text{nt} | Ti             |                     |                        |
| Ru-Ta 100:0        | 0.0005         | 7.81                | 1.12                   |
| Ru-Ta 70:30        | 0.0008         | 11.98               | 1.72                   |
| Ru-Ta 50:50        | 0.0004         | 13.45               | 1.93                   |
| Ru-Ta 30:70        | 0.0007         | 11.54               | 1.65                   |
| PbO\(_2/\text{Ta}_2\text{O}_5/\text{TiO}_2,\text{nt} | Ti             |                     |                        |
| Pb-Ta 100:0        | 0.0008         | 12.97               | 1.86                   |
| Pb-Ta 70:30        | 0.0002         | 3.77                | 0.54                   |
| Pb-Ta 50:50        | 0.0002         | 3.71                | 0.53                   |
| Pb-Ta 30:70        | 0.0004         | 6.58                | 0.94                   |
| TaO\(_2/\text{TiO}_2,\text{nt} | Ti             |                     |                        |
| Ta                 | 0.0007         | 11.15               | 1.60                   |
| TiO\(_2,\text{nt} |                | 3.12                | 0.45                   |
| Ti                 | 0.0003         | 5.00                | 0.72                   |

### Electrochemical degradation of amoxicillin using modified electrodes

Figure 7 shows the polarization curves of AMX in 0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\), where there are two characteristic zones related to kinetic control (from 0 to 1 V vs. Ag | AgCl 3M NaCl) and mix control (from 1 to 3 V vs. Ag | AgCl 3M NaCl). The mass transport zone was not defined by the possible effect of the nanotubular structure of TiO\(_{2,\text{nt}}\), which has different active sites without stabilizing a limit current density. After 2 V vs.
Ag | AgCl 3M NaCl, there is an important increment in the current density by the electrolysis of water; at the same time, there are oxidant agents which are involved in the electrooxidation of AMX in acid media, such as hydroxyl radicals (Auguste et al. 2016; León et al. 2020). The major current density achieved at 3 V vs. Ag | AgCl 3M NaCl was shown by Ir-Ta 100:0 (0.5 mA cm⁻²) followed by Ir-Ta 30:70 (0.18 mA cm⁻²) > Ru-Ta 100:0 (0.16 mA cm⁻²) > Ir-Ta 50:50 (0.14 mA cm⁻²) > Ru-Ta 70:30 (0.12 mA cm⁻²) > Ru-Ta 30:70 (0.08 mA cm⁻²) > TiO₂,nt ≅ Pb-Ta 70:30 ≅ Pb-Ta 50:50 ≅ Ir-Ta 70:30 ≅ Ta ≅ (0.07 mA cm⁻²) > Ru-Ta 50:50 ≅ Pb-Ta 30:70 ≅ Ti (0.5 mA cm⁻²) > Pb-Ta 100:0 (0.1 mA cm⁻²).

With these results, 100 μA cm⁻² was selected to be sure that electrooxidation of AMX took place where the generation of hydroxyl radicals is developed (Herrada et al. 2018, 2020; León et al. 2020), with the highest oxidation redox state of the Ir (Eq. 6), Ru (Eq. 8), and Pb (Eq. 10). Figure 8 shows the removal efficiency of AMX (η%) in 0.1 mol L⁻¹ H₂SO₄ every 10 min to 120 min of electrolysis. In this comparison, after 10 min, the highest removal efficiency of AMX was shown with Pb-Ta 50:50 (25.57%) modified by Pb-Ta 50:50 (44.71%) which shows the highest current density in the polarization curve (Fig. 7c) followed by Pb-Ta 30:70 (38.67%) > Ir-Ta 50:50 (34.81%) > Ru-Ta 70:30 (28.68%) > Ta (22.91%) > Ru-Ta 70:30 (22.50%) > Ir-Ta 70:30 (20.81%) > Ru-Ta 30:70 (17.59%) > Ru-Ta 100:0 (14.60%) > Ir-Ta 30:70 (10.94%) > Pb-Ta 100:0 (0%). In the case of the naked Ti, it shows a removal efficiency of 19.23%.

Therefore, in this kind of surface, the inclusion of Ta plays an important role as it acts as a protonic conductor (Comninellis and Vercesi 1991; León et al. 2020) to promote the electrooxidation of AMX by the major generation of HO⁻ radicals when the protons are retained over the modified surface since, without Ta, the Pb-Ta 100:0 did not show any removal efficiency. Despite the Pb-Ta 50:50|TiO₂,nt|Ti and Pb-Ta 30:70 |TiO₂,nt|Ti electrode systems showed AMX removal, their removal efficiencies remain below from that achieved by the IrO₂-Ta₂O₅ |Ti and RuO₂-Ta₂O₅ |Ti electrode systems in acidic aqueous medium (i.e., 0.1 mol L⁻¹ H₂SO₄) (León et al. 2020). A new revision of the CV responses compiled in Fig. 6 revealed that the H₂O electroactivation on the anatase TiO₂,nt phase should occur at a potential more cathodic than for the other metallic oxide (MO). This difference in the HO⁻ radical generation (Eq. 11 and Eq. 12) seems to conduct to the HO⁻ radical deactivation.

Fig. 5 Cyclic voltammetry of naked Ti and modified TiO₂,nt|Ti by the different concentration relations of Ir (a), Ru (b), and Pb (c) without and with Ta with the concentration relation of 30:70 (i), 50:50 (ii), and 70:30 (iii) electrodes in 0.1 mol L⁻¹ H₂SO₄ at 20 mV s⁻¹ and 293 K.
via Eq. 13, which resembles the $^\cdot$OH radical deactivation typically observed at photocatalytic anatase TiO$_2$ systems generating H$_2$O$_2$ (Eq. 14) (Zhang and Nosaka 2014).

$$\begin{align*}
\text{H}_2\text{O} & + \text{MO|TiO}_2(\text{H}_2\text{O})_{\text{ads}} \rightarrow \text{ads}(\text{H}_2\text{O})\text{MO|TiO}_2(\cdot\text{OH})_{\text{ads}} \\
& + \text{H}^+ + e^- \\
& \text{ads}(\cdot\text{OH})\text{MO|TiO}_2(\cdot\text{OH})_{\text{ads}} \rightarrow \text{ads}(\cdot\text{OH})\text{MO|TiO}_2(\cdot\text{OH})_{\text{ads}} \\
& \text{ads}(\cdot\text{OH})\text{MO|TiO}_2(\cdot\text{OH})_{\text{ads}} \rightarrow \text{ads}(\cdot\text{OH})\text{MO|TiO}_2(\cdot\text{OH})_{\text{ads}} \\
& 2\cdot\text{OH} \rightarrow \text{H}_2\text{O}_2
\end{align*}$$

In Table 3, there is a comparison of COD, TOC, CT, and CI. In the case of the COD, the lowest values in the modified TiO$_2$,nt|Ti by Ir were for the Ir-Ta 50:50 (3.29 ± 1.47 mg L$^{-1}$); by Ru were for the Ru-Ta 50:50 (4.75 ± 0.35 mg L$^{-1}$) and for Ru-Ta 70:30 (5.17 ± 1.65 mg L$^{-1}$); and by Pb were for the Pb-Ta 30:70 (6.00 ± 1.41 mg L$^{-1}$) and for Pb-Ta 50:50 (6.75 ± 0.35 mg L$^{-1}$). In the case of TOC, CT and CI were not a major difference; they were on average 5, 5, and 0.3 mg L$^{-1}$ respectively.

In the case of the energy consumption (Table 4), the highest values in the modified TiO$_2$,nt|Ti were the Ru-Ta 30:70 and Pb-Ta 100:00 (0.223 ± 0.018 mWh m$^{-3}$), and the lowest were Ir-Ta 100:0 (0.018 ± 0.001 mWh m$^{-3}$) < TiO$_2$,nt|Ti (0.031 ± 0.031 mWh m$^{-3}$) < Pb-Ta 70:30 (0.040 ± 0.004 mWh m$^{-3}$) < Pb-Ta 50:50 (0.041 ± 0.004 mWh m$^{-3}$), where the last one showed the highest removal efficiency of AMX (44.71%, Fig. 8c) with the lowest specific energy consumption (8.69 ± 0.78 kWh Kg COD$^{-1}$), and the average instant current efficiency of 26.67 ± 9.19%, in comparison with the others naked and modified surfaces of TiO$_2$,nt|Ti.

**Conclusions**

The results obtained in this study indicated that titania nanotubes were effectively constructed after 1 h of anodization. These nanotubular structures showed a diameter of 50.10 ±
7.11 nm. From EDX analyses, the prepared TiO$_2$ nanotubes showed a 1:2 ratio for the Ti and O, respectively, and Raman studies suggested the formation of anatase and rutile phases during anodization.

**Fig. 7** Polarization curves of AMX in 0.1 mol L$^{-1}$ H$_2$SO$_4$ using cronoamperometries by 15 min in the presence of naked Ti and modified TiO$_{2,nit}$Ti by the different concentration ratios of Ir (a), Ru (b), and Pb (c) without and with Ta with the concentration ratio of 30:70 (i), 50:50 (ii), and 70:30 (iii) electrodes at 293 K.

**Fig. 8** Degradation efficiencies of AMX in 0.1 mol L$^{-1}$ H$_2$SO$_4$ every 10 min to 120 min of electrolysis using naked Ti and modified TiO$_{2,nit}$Ti by the different concentration relations of Ir (a), Ru (b), and Pb (c) without and with Ta with the concentration relation of 30:70, 50:50, and 70:30 electrodes at 293 K.
This surface was modified with a heterogeneous electrodeposited film with different concentrations of IrO\(_2\)-Ta\(_2\)O\(_5\), RuO\(_2\)-Ta\(_2\)O\(_5\), and PbO\(_2\)-Ta\(_2\)O\(_5\), which increased the electroactive area and roughness compared to the ones shown by naked TiO\(_2\),nT. SEM images showed complete coverage of all of these deposits over the nanotubes array. Ir-Ta deposits showed an electrodeposit with coliform morphology, which suggests the filling of TiO\(_2\),nT came out from them, as it has been reported in the literature. Ir-Ta and Pb-Ta deposits showed the biggest potential window in acidic conditions at both low and with high scan rates, and Ru and Ir electrocatalysts had a similar electrochemical behavior due to their physicochemical characteristics as metallic conductivity and rutile crystalline structure.

During the electrochemical analysis, different redox processes were obtained, in the case of IrO\(_2\)-Ta\(_2\)O\(_5\) | TiO\(_2\),nT showed the Ir\(^{+2}/\)Ir\(^{4+}\) and Ir\(^{4+}/\)Ir\(^{5+}\), in the case of RuO\(_2\)-Ta\(_2\)O\(_5\) | TiO\(_2\),nT showed the Ru\(^{3+}/\)Ru\(^{4+}\) and Ru\(^{4+}/\)Ru\(^{6+}\), and in the case of PbO\(_2\)-Ta\(_2\)O\(_5\) | TiO\(_2\),nT showed the Pb\(^{+2}/\)Pb\(^{+3}\) and Pb\(^{+3}/\)Pb\(^{+4}\). From polarization curves, 100 \(\mu\)A cm\(^{-2}\) was selected to be sure that electrooxidation of AMX took place where the generation of hydroxyl radicals is developed (Herrada et al. 2018, 2020; León et al. 2020), with the highest oxidation redox state of the Ir (Eq. 6), Ru (Eq. 8), and Pb (Eq. 10). In the removal studies, the highest removal efficiency of AMX was

### Table 3

| Electrodes | AMX | COD (mg L\(^{-1}\)) | TOC (mg L\(^{-1}\)) | CT (mg L\(^{-1}\)) | CI (mg L\(^{-1}\)) |
|------------|-----|---------------------|---------------------|-------------------|-------------------|
| IrO\(_2\)-Ta\(_2\)O\(_5\)| | 11.50 ± 0.71 | 4.91 ± 0.01 | 5.18 ± 0.01 | 0.27 ± 0.01 |
| Ta\(_2\)O\(_5\)| | | | | |

This table shows the chemical organic demand (COD), total organic carbon (TOC), carbon total (CT), and carbon inorganic (CI) of AMX in 0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\) after 120 min in the presence of different naked Ti and modified TiO\(_2\),nT by Ir, Ru, and Pb without and with Ir, Ru, and Pb in presence or not of Ta.

### Table 4

| Electrodes | EC (Wh m\(^{-3}\)) | \(E_{\text{sp}}\) (kWh Kg COD\(^{-1}\)) | ICE (%) |
|------------|-------------------|-------------------------------|--------|
| IrO\(_2\)-Ta\(_2\)O\(_5\)| 0.018 ± 0.001 | 9.04 ± 0.11 | 14.13 ± 3.99 |
| Ta\(_2\)O\(_5\)| | | |

This table shows the energy consumption (EC), specific energy consumption (\(E_{\text{sp}}\)), and instant current efficiency (ICE) of AMX in 0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\) after 120 min in the presence of different naked Ti and modified TiO\(_2\),nT by Ir, Ru, and Pb without and with Ir, Ru, and Pb in the presence or not of Ta.
shown with Pb-Ta 50:50 (44.71%), which achieved the highest current densities in the polarization curve, but with a rather high COD (9 mg L\(^{-1}\)), which suggest a low degradation of AMX.

However, with the Pb-Ta 30:70, the second-highest AMX removal efficiency (38.6%) was achieved, and a low COD was obtained, which suggests a higher degradation achieved by this oxides mixture. These mixtures had a low energy consumption and specific energy consumption, with an average instant current efficiency. Although both the Pb-Ta 50:50/TiO\(_2\) and Pb-Ta 30:70/TiO\(_2\) showed effective removal efficiencies, they are the lowest that were reported before using IrO\(_2\)-Ta\(_2\)O\(_5\)|Ti and RuO\(_2\)-Ta\(_2\)O\(_5\)|Ti in acid (0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\)) by the OH radical deactivation typically observed at anatase TiO\(_2\) systems generating H\(_2\)O\(_2\). Anyway, these kinds of materials are another alternative to be used in the electrooxidation of AMX in acidic conditions, and it has not been reported before.

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Author contribution JShB constructed all the modified electrodes, obtained the electrochemical characterization of the naked and modified surfaces, and obtained the electrochemical degradation of AMX and the COD analysis. MC proposed the methodology to construct the TiO\(_2\)\(_{nt}\)|Ti and its modification with Pb. AS improved the methodology to obtain the TiO\(_2\)\(_{nt}\)|Ti and reviewed the fundamental papers to write this paper. FE obtained all the SEM analysis. JM obtained all the Raman analysis. JT obtained all the TOC, CT, and CI. JC and YM got the equipment and chemical compounds to get the COD, TOC, CT, and CI. MC and JM got the financial support by the project PN 2016-3620 and FOINS 3838 to develop this research. EB proposed the idea of this research, organized, wrote, and made the conjunction of all the discussions of results with all the co-authors. All authors reviewed and approved the final manuscript.

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