

Sequential electrochemical treatment of dairy wastewater using aluminum and DSA-type anodes

Brenda Borbón · Mercedes Teresita Oropeza-Guzman ·
Enric Brillas · Ignasi Sirés

Received: 19 February 2014 / Accepted: 10 March 2014 / Published online: 27 March 2014
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Abstract Dairy wastewater is characterized by a high content of hardly biodegradable dissolved, colloidal, and suspended organic matter. This work firstly investigates the performance of two individual electrochemical treatments, namely electrocoagulation (EC) and electro-oxidation (EO), in order to finally assess the mineralization ability of a sequential EC/EO process. EC with an Al anode was employed as a primary pretreatment for the conditioning of 800 mL of wastewater. A complete reduction of turbidity, as well as 90 and 81 % of chemical oxygen demand (COD) and total organic carbon (TOC) removal, respectively, were achieved after 120 min of EC at 9.09 mA cm^{-2} . For EO, two kinds of dimensionally stable anodes (DSA) electrodes (Ti/IrO₂-Ta₂O₅ and Ti/IrO₂-SnO₂-Sb₂O₅) were prepared by the Pechini method, obtaining homogeneous coatings with uniform composition and high roughness. The ·OH formed at the DSA surface from H₂O oxidation were not detected by electron spin resonance. However, their indirect determination by means of H₂O₂ measurements revealed that Ti/IrO₂-SnO₂-Sb₂O₅ is able to produce partially physisorbed radicals. Since the characterization of the wastewater revealed the presence of indole derivatives, preliminary bulk electrolyses were done in ultrapure water containing 1 mM indole in sulfate and/or chloride media. The performance of EO with the Ti/IrO₂-Ta₂O₅ anode was evaluated from the TOC removal and the UV/Vis absorbance decay.

The mineralization was very poor in 0.05 M Na₂SO₄, whereas it increased considerably at a greater Cl⁻ content, meaning that the oxidation mediated by electrogenerated species such as Cl₂, HClO, and/or ClO⁻ competes and even predominates over the ·OH-mediated oxidation. The EO treatment of EC-pretreated dairy wastewater allowed obtaining a global 98 % TOC removal, decreasing from 1,062 to <30 mg L⁻¹.

Keywords Dairy wastewater · DSA electrode · Electrocoagulation · Electron spin resonance · Electro-oxidation · Indole · Sequential water treatment

Introduction

Wastewater from animal operations has a negative impact on environment. In particular, great concerns arise from dairy wastewater because it is characterized by high organic matter content that is hardly biodegradable, which can damage the natural water streams in case of uncontrolled discharge. Refractory alcohols, carboxylic acids, and indole derivatives, among others, are usually identified in such effluents (Laor et al. 2008). Furthermore, studies on the water footprint of animal products estimate that up to 1,000 L H₂O are necessary to produce 1 L of milk (Hoekstra 2010), which entails dramatic effects for the living beings in cases of release of untreated wastewater. Due to the large volume of effluents with variable characteristics generated in dairies, the dairy industry is considered as the most polluting among the food industries (Vourch et al. 2008).

In Mexico, the National Water Commission (Conagua) has reported that only 20 % of contaminated wastewater is treated before discharge to lakes, lagoons, and coastal areas (Comisión Nacional del Agua (Conagua) 2010). A case of particular interest is Baja California, which is considered as one of the Mexican states with lower drinking water supply,

Responsible editor: Philippe Garrigues

B. Borbón · M. T. Oropeza-Guzman
Centro de Investigación y Desarrollo Tecnológico en Electroquímica,
Unidad Tijuana, Carretera Tijuana-Tecate km 26.6, Consorcio
Tecnológico de Baja California, 22444 Tijuana, B.C., Mexico

E. Brillas · I. Sirés (✉)
Laboratori d'Electroquímica dels Materials i del Medi Ambient,
Departament de Química Física, Facultat de Química, Universitat de
Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain
e-mail: i.sires@ub.edu

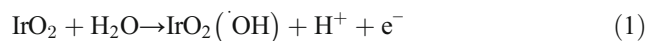
being further aggravated by the large water consumption from the expansive industrial sector, including the milk-producing industry. Therefore, water reuse is rather interesting in dairy industry since it would allow the decrease of both the water needs for cleaning dairies and herds and the risks for infection that arise from lagooning.

Dairy wastewater is most typically treated by bioremediation and physicochemical methods such as coagulation/flocculation. Unfortunately, the former requires large spaces and long times, whereas the latter presents high reagent costs and poor removal of soluble chemical oxygen demand (COD). On the other hand, at present, electrochemical technologies such as electrocoagulation (EC) and the electrochemical advanced oxidation processes (EAOPs) are receiving great attention for the removal of organic pollutants from waters, since they allow significant decontamination percentages with high efficiencies in compact reactors that only require simple equipments for operation and can be carried out at moderate costs (Anglada et al. 2009; Brillas et al. 2009; Panizza and Cerisola 2009).

EC is a primary wastewater treatment for inducing the controlled electrogeneration of flocculants/coagulants on site, usually under the application of a constant current. It is a complex process involving several chemical and physical phenomena with the formation of iron or aluminum cations from the dissolution of the corresponding sacrificial anode(s) and the simultaneous production of OH⁻ anions by cathodic reduction of water. The polymeric metal hydroxides formed act as excellent coagulating agents to favor the removal of dissolved, colloidal, or suspended matter, eventually yielding great percentages of removal of color and turbidity. Coagulation mainly occurs by destabilization, once the metal cations combine with the negatively charged particles moving towards the anode by electrophoretic motion (Mollah et al. 2001; Martínez-Huitle and Brillas 2009). EC has been successfully tested to treat wastewaters from several industries (Szpyrkowicz 2005; Zodi et al. 2010; Cotillas et al. 2013), but only since recently it has been applied to the treatment of simulated and real dairy wastewater using iron/steel (Ayhan Şengil and Özacar 2006; Kushwaha et al. 2010) or aluminum (Tchamango et al. 2010; Bensadok et al. 2011) anodes. The latter have led to 60–80 and 96–100 % of COD and turbidity removal, respectively.

EAOPs can be applied as an effective post-treatment for the controlled electrogeneration of oxidizing species on site. Among them, electro-Fenton process (Anotai et al. 2011; Randazzo et al. 2011; Dirany et al. 2012) and electro-oxidation (EO) (Comninellis 1994; Tahar and Savall 1998; Marselli et al. 2003; Martínez-Huitle et al. 2004; Panizza and Cerisola 2004; Polcaro et al. 2004; Panizza and Cerisola 2006; Butrón et al. 2007; Cañizares et al. 2007; Panizza and Cerisola 2007; Hammami et al. 2008; Özcan et al. 2008; Ribeiro et al. 2008; Beteta et al. 2009; Flox et al. 2009; Hamza et al. 2009;

Liu et al. 2009; Dirany et al. 2010; Fierro et al. 2010; Sirés et al. 2010; Bezerra Rocha et al. 2011; Souza Duarte et al. 2011; Flox et al. 2012; Chaiyont et al. 2013; El-Ghenymy et al. 2013a, b) are the most widespread technologies for treating synthetic solutions and real waters. In particular, EO turns out to be very appealing because it allows the ·OH-mediated decontamination of polluted wastewaters in all the pH range. Boron-doped diamond (BDD) anodes exhibit the highest performance (Marselli et al. 2003; Polcaro et al. 2004; Butrón et al. 2007; Cañizares et al. 2007; Panizza and Cerisola 2007; Hammami et al. 2008; Özcan et al. 2008; Beteta et al. 2009; Hamza et al. 2009; Liu et al. 2009; Dirany et al. 2010; Bezerra Rocha et al. 2011; Flox et al. 2012; El-Ghenymy et al. 2013a, b), but less expensive alternatives with a high oxidation power such as PbO₂ (Tahar and Savall 1998; Panizza and Cerisola 2004; Flox et al. 2009; Sirés et al. 2010) and SnO₂ (Comninellis 1994; Panizza and Cerisola 2009) have been proposed. SnO₂ electrodes doped with antimony are easy to produce, but they have a limited lifetime. Lately, special attention has been paid to the manufacture of dimensionally stable anodes (DSA)-type electrodes due to their stability and acceptable oxidation ability. SnO₂-based DSA electrodes with an IrO₂ interlayer (Ti/IrO₂-SnO₂-Sb₂O₅) are more stable than the raw ones and are able to produce physisorbed hydroxyl radicals that allow the oxidation of organic compounds (Chaiyont et al. 2013). Also the metal and mixed-metal oxide electrodes based on RuO₂ (Panizza and Cerisola 2006; Ribeiro et al. 2008) and IrO₂ (Comninellis 1994; Panizza and Cerisola 2009; Fierro et al. 2010) are widely used in environmental electrochemistry because of their outstanding mechanical stability, long service lifetime, reasonable electrocatalytic activity, low cost, easiness of preparation, and successful scale-up. They have long been applied in the chlor-alkali industry thanks to their catalytic efficiency. IrO₂-based DSA is especially interesting because it exhibits high corrosion resistance, being only slightly inferior to RuO₂ in terms of electrocatalysis. IrO₂ is known to be a good electrocatalyst for the oxidation of organic compounds thanks to the formation of adsorbed hydroxyl radicals (Fierro et al. 2010):



IrO₂(OH) can be further oxidized to a covalently bound species (chemisorbed active oxygen). The most common coatings incorporate Ta₂O₅ as a stabilizing agent (Martínez-Huitle et al. 2004; Panizza and Cerisola 2009).

The purpose of this work is to assess the combination of two electrochemical water treatments, namely EC with Al anodes for the removal of solids in order to separate a large fraction of organic matter and EO with DSA anodes for the destruction of the dissolved organic matter remaining in the pretreated wastewater, aiming at its potential application in the conditioning of dairy wastewater. Most EO experiments were

performed with purpose-made Ti/IrO₂-Ta₂O₅ by using the polymer precursor method (PPM) known as the Pechini method (Pechini and Adams 1967), although Ti/IrO₂-SnO₂-Sb₂O₅ were prepared as well for comparison. Among the sol-gel methods, the PPM is advantageous because it is simple, not sensitive to water, and gives rise to smoother surfaces and a more uniform composition without a mud-cracked surface appearance (Bitencourt et al. 2010). In particular, the Pechini-derived electrodes exhibit a longer lifetime (Forti et al. 2001; Bitencourt et al. 2010). The morphological and electrocatalytic properties were assessed by surface (scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDX) and atomic force microscopy (AFM)) and electrochemical (linear sweep voltammetry (LSV) and cyclic voltammetry (CV)) analysis. Their ability to generate hydroxyl radicals has also been surveyed by two different techniques: (1) using a radical scavenger followed by electron spin resonance (ESR) analysis and (2) by spectrophotometric UV/Vis analysis of the Ti(IV)-H₂O₂ complex. Preliminary bulk electrolyses were performed with the model compound indole (i.e., a major component of the actual dairy wastewater of interest, as experimentally verified) in ultrapure water using NaCl and/or Na₂SO₄ media. Finally, the performance of the sequential method was investigated by applying EO to previously EC-pretreated actual wastewater.

Materials and methods

Chemicals

Indole was of reagent grade purchased from Sigma-Aldrich (purity ≥99 %). 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) for ESR spectroscopy from Fluka (purity ≥99 %) was used as

trapping agent for ·OH detection. Anhydrous sodium sulfate and sodium chloride used as background electrolytes were of analytical grade purchased from Acros Organics. Reagent grade sulfuric acid and sodium hydroxide from VWR International were used to adjust the initial pH either to 3.0 or 8.0 whenever required. All the other chemicals used were either of HPLC or analytical grade from Sigma-Aldrich, Fluka, and Acros Organics. All solutions, except those of wastewater, were prepared with high-purity water obtained from a Millipore Milli-Q system with resistivity >18 MΩ cm.

Physicochemical characterization of the dairy wastewater

The wastewater was obtained from a dairy situated in km 58 of the Rosarito-Ensenada highway, in the heart of an important Mexican dairy region. About 14,000 L of milk are daily produced. The wastewater mainly results from cleaning of either cattle before milking, milk-sucking instruments, and cowsheds, and is further conveyed to a lagoon. The characteristics of the wastewater used in this work are summarized in Table 1. Note that the BOD₅/COD ratio is 0.39, which suggests that it is a hardly biodegradable effluent because of the presence of many toxic molecules. Partitioning with organic solvents was used to extract the organic compounds from the water, which were subsequently analyzed by infrared spectroscopy. Indole derivatives, as well as alcohols, esters, carboxylic acids, and *N*-containing compounds were present in the samples, which agrees with characterization tests reported by Laor et al. (2008).

Preparation of DSA electrodes

Ternary oxide electrodes (Ti/IrO₂-SnO₂-Sb₂O₅) were obtained by PPM deposition onto pretreated Ti mesh as explained by

Table 1 Characteristics of the dairy wastewater under study and main changes occurring upon application of the EC process for 120 min at different current densities

Parameter	Dairy wastewater	After 120 min of EC at 3.63 mA cm ⁻²	After 120 min of EC at 9.09 mA cm ⁻²
pH	8.27		
Conductivity (mS cm ⁻¹)	2.36		
COD (mg O ₂ L ⁻¹)	3,859	730	395
TOC (mg C L ⁻¹)	1,062	741	198
BOD ₅ (mg O ₂ L ⁻¹)	1,517		
Total suspended solids (TSS) (mg L ⁻¹)	6		
Sedimentable solids (SS) (mg L ⁻¹)	1,988		
Turbidity (NTU)	3,900	3	9
Free chlorine (mg Cl ₂ L ⁻¹)	16.5		
[Cl ⁻] (mg L ⁻¹)	1,131		
[NO ₂ ⁻] (mg L ⁻¹)	0.4		
[NO ₃ ⁻] (mg L ⁻¹)	1.5		
[NH ₄ ⁺] (mg L ⁻¹)	177		

Chaoyont et al. (2013). On the other hand, the Ti/IrO₂-Ta₂O₅ electrodes were also prepared by PPM using a pretreated Ti mesh as the substrate. In this case, the precursor aqueous solution contained H₂IrCl₆ and TaCl₅. The mixture was then applied to the support with a brush. Afterwards, the electrodes were heated at 100 °C for 10 min in a furnace in order to induce the polymerization of the precursor. This procedure was repeated three times. After the final coating, the electrodes were maintained at 550 °C for 30 min in order to ensure the calcination of the polymer and formation of the metal oxides that confer enough stability to the pieces.

Electrolytic system for electrocoagulation

All the EC trials were conducted in an open, undivided rectangular glass cell of 1-L capacity. A 55-cm² (26.7 g) aluminum plate and a large surface iron mesh were employed as monopolar anode and cathode, respectively. All the experiments were performed in batch, operating galvanostatically by using direct current density (*j*) of 3.63 or 9.09 mA cm⁻² (values referred to the anodic surface area).

Solutions of 800 mL containing the wastewater and 0.4 g NaCl as supporting electrolyte were electrolyzed for 120 min in 30-min intervals allowing sedimentation for 1 h between every two consecutive electrolyses. The addition of chloride intended to inhibit or slow down the anode passivation, which has been typically observed for Al due to the formation of an isolating, compact oxide interlayer.

Electrolytic system for electro-oxidation

All the EO trials were conducted in an open, undivided cylindrical glass cell of 150-mL capacity with a double jacket for circulation of external thermostated water to regulate the solution temperature at 25 °C. The anode was usually a 2.5 cm² Ti/IrO₂-Ta₂O₅ electrode, although Ti/IrO₂-SnO₂-Sb₂O₅ was used for comparison in some trials. The cathode was a Pt wire. The interelectrode gap was about 1 cm. All the experiments were performed at constant current, with vigorous stirring of the solution by means of a magnetic bar at 800 rpm to ensure mixing and the transport of reactants towards/from the electrodes.

Electrolyses were firstly carried out in ultrapure water. Solutions of 100 mL containing 100 mg L⁻¹ total organic carbon (TOC) of indole and Na₂SO₄ and/or NaCl as supporting electrolyte were treated at different currents at pH 3.0 or 8.0. The ability of the DSA electrodes to produce ·OH from H₂O oxidation was assessed in ultrapure water as well by spin-trapping and UV spectrophotometry. The former was conducted by using DMPO as the trapping agent (Marselli et al. 2003). Low concentrations of ·OH can be detected by firstly forming a spin adduct that exhibits a much longer lifetime than the radical alone and then obtaining the ESR

spectrum of samples withdrawn at different electrolysis times. Solutions of 10 mM DMPO in 0.05 M Na₂SO₄ at pH 3.0 or 8.0 were electrolyzed galvanostatically at 0.1, 1, 10, and 59 mA cm⁻² for 10 and 60 min using a system analogous to that described for EO but with a lower volume (10 mL) and smaller DSA area (0.2 cm²). In the second method, the H₂O₂ production was assessed at different times from electrolyses of 0.05 M Na₂SO₄ performed potentiostatically using Ag|AgCl (3.5 M KCl) and a Pt wire as the reference electrode and counter electrodes, respectively.

Solutions of 100 mL of EC-pretreated dairy wastewater were treated using the same setup described for indole solutions, but employing a 6.6 cm² DSA anode instead.

Instruments and analysis procedures

EC was performed using a 6552A DC power supply from Agilent, whereas EO was conducted with an Amel 2063 potentiostat-galvanostat. All the electrolyses were performed at room temperature by means of thermostated cells or water baths. The solution pH was measured with a Crison 2000 pH meter. Conductimetric measurements were carried out with a Cole-Parmer instrument. An Imhoff tank was used to analyze the sedimentable solids (SS). A Hach DRB200 Digital Reactor Block and a Hach DR/890 portable colorimeter were used for measuring COD. The latter equipment was also used for analyzing the total suspended solids (TSS), free and total chlorine, and turbidity. BOD₅ was assessed from the measurement of the dissolved oxygen based on the Winkler test. The inorganic anions contained in the wastewater were determined by ion chromatography upon injection into a Kontron HPLC model 465 coupled with a Waters 432 conductometric detector. A Waters IC-PAK Anions 150 mm×4.6 mm (i.d), column with 10-nm particle size, at 40 °C was used. The mobile phase containing boric acid, sodium gluconate, sodium tetraborate, acetonitrile, butanol, and glycerine was eluted at 2.0 mL min⁻¹. The analyses were carried out according to EPA 9056 method using PC Integration Pack from Kontron. The NH₄⁺ content was determined by flow injection analysis technique based on colorimetry with blue of indole-phenol employing an ALPKEM model Flow Solution IV.

The DSA electrodes were extensively characterized by surface and electrochemical analyses. The morphology was examined by thermal field emission SEM using a JSM 6500F with an accelerating voltage of 15 kV equipped with an Oxford Inca 300 EDX analyzer. In some cases, a JSM 5400LV coupled to EDX analyzer was used instead. Data collection time was always 5 min. AFM was alternatively employed using a Nanosurf Easyscan 2 microscope working in the AC imaging mode (tapping mode) in air with silicon probes. For the electrochemical characterization, LSV and CV were carried out with an Autolab PGSTAT30 instrument, using a purpose-built, three-electrode undivided glass cell

containing 50 mL of supporting electrolyte at pH 3.0 or 8.0 at room temperature, with a large area platinum gauze and Ag|AgCl (3.5 M KCl) mounted in a Luggin capillary as the counter and reference electrodes, respectively. The exposed area of the working DSA electrode was 1.28 cm². All potentials in this work are referred to Ag|AgCl (3.5 M KCl).

The ability of the DSA electrodes to produce ·OH from H₂O oxidation was analyzed by spin trapping and UV spectrophotometry. For the former, 400 μL of samples withdrawn upon electrolysis of DMPO were placed into a vial to be frozen with dry ice for ensuring preservation until analysis. In order to assess the presence of the DMPO spin adduct, the ESR spectra of samples were recorded at room temperature with a Bruker ESP300E spectrometer controlled by Win-EPR 2.3 SimFonia software. The conditions for the measurement were: X Band; 100 kHz modulation frequency with 1.5 G application; microwave power, 10 mW; central magnetic field, 3,350 G; and sweep width, 100 G. On the other hand, the concentration of H₂O₂ formed in electrolyzed solutions from ·OH recombination was determined from the light absorption of its Ti(IV) colored complex at λ=408 nm using a Shimadzu 1800 UV/Vis spectrophotometer thermostated at 35 °C (Welcher 1975).

The mineralization of either indole solutions or wastewater was usually monitored from their TOC decay, measured with a Shimadzu VCSH TOC analyzer. Reproducible TOC values with an accuracy of ±1 % were found by injecting 50-μL aliquots into the analyzer. The changes in the UV/Vis spectrum of indole solutions upon EO were monitored from measurements between 200 and 800 nm with the previous spectrophotometer. For both kinds of analyses, samples were withdrawn at regular time intervals.

Results and discussion

Electrocoagulation of dairy wastewater

Based on the large content of solids in the wastewater under study, EC was considered as a suitable pretreatment method. Indeed, after 120 min of electrolysis, the initially turbid water became transparent, which can be confirmed by the turbidity measurements collected in Table 1 at two different current densities. A closer look to the measurements taken at different time periods (not shown) allowed concluding that the percentages of turbidity and COD removal already attained an almost constant value after 60 min. For example, at 3.63 mA cm⁻², turbidity decreased by 82, 95, and 99.9 % at 30, 60, and 120 min, respectively. Similarly, at those times, COD was reduced by 65, 80, and 81 %. Figure 1a shows the progressive clarification of the wastewater samples at 3.63 mA cm⁻², changing from initial brownish to final pale yellow. This transition can be basically related to the removal of suspended

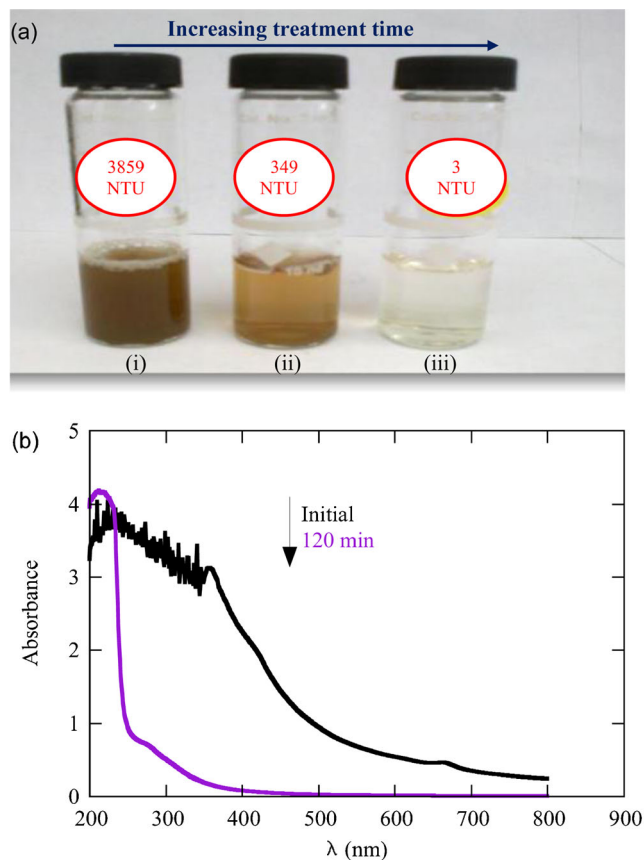


Fig. 1 a Photograph of (i) initial dairy wastewater and samples withdrawn after (ii) 15 and (iii) 120 min of EC pre-treatment at 3.63 mA cm⁻². b UV/Vis spectra of the wastewater before and after the process

and sedimentable solids, which in turn allows justifying the progressive abatement of COD and TOC also reported in Table 1. Furthermore, EC also allowed a remarkable removal of aromatic pollutants. Figure 1b evidences that the UV/Vis spectrum of the raw wastewater was characterized by a high absorbance from 200 to 500 nm as expected from an effluent with a large content of toxic (i.e., benzenic) and/or colored pollutants. According to the aforementioned characterization of the wastewater (“Physicochemical characterization of the dairy wastewater” section) as well as the typical unpleasant odor arising from the presence of cow manure, the presence of indole derivatives can be certainly ensured. These are mainly formed during the decomposition of tryptophan and tryptophan-containing proteins. Figure 1b also shows that after the application of the EC process at 3.63 mA cm⁻² for 120 min, a large percentage of these compounds had disappeared since the absorbance at 254–280 nm was much lower, and for λ>400 nm it was almost negligible. The solution pre-eminently absorbed at 210 nm, which is related to the presence of aliphatic molecules.

The investigation at two current densities aimed at finding the most convenient condition for the removal of particulate matter. The results shown in Table 1 at the end of the EC process revealed that COD and TOC contents were about 50

and 25 % lower, respectively, at higher current density, whereas turbidity was almost the same in both cases. Electrolysis at 9.09 mA cm^{-2} was therefore more effective to induce the coagulation of solids and colloidal matter via charge neutralization, which directly involved a quicker decrease of turbidity and organic matter content. These results allowed concluding that EC is an optimal pretreatment method to further apply a secondary treatment such as EO with DSA electrodes.

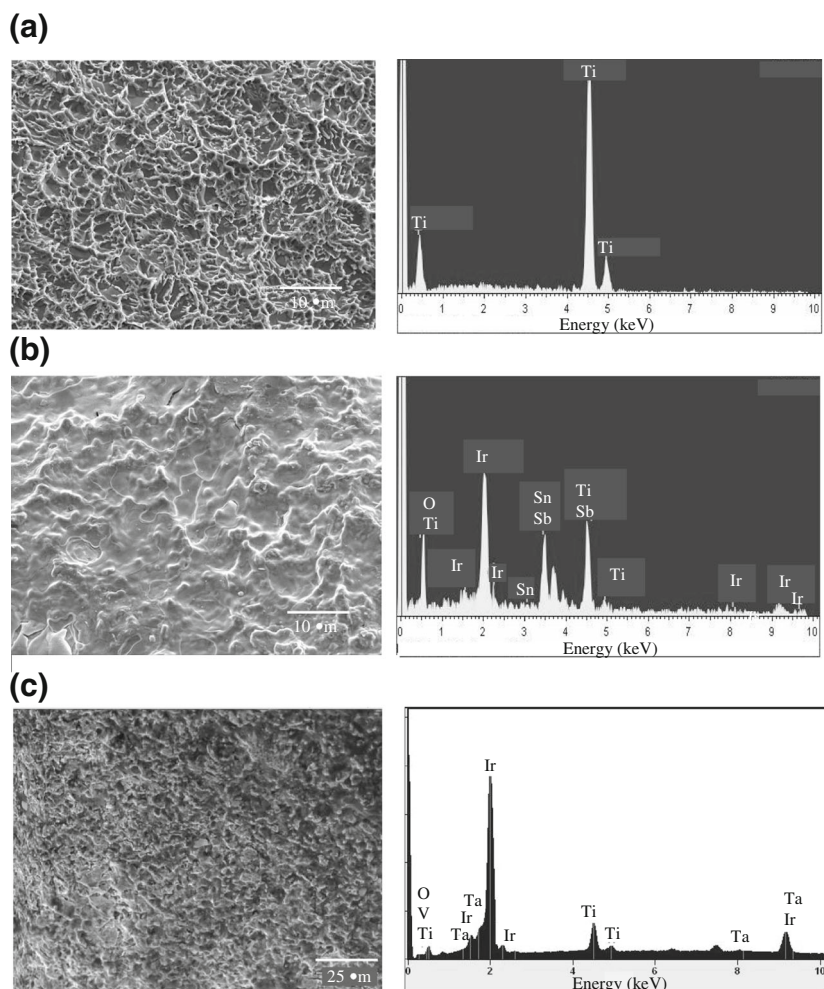
Characterization of manufactured DSA electrodes

Figure 2 presents the SEM-EDX surface analyses carried out for studying the morphology and surface composition of DSA electrodes prepared by PPM as described in the “Preparation of DSA electrodes” section. A pure Ti mesh was used as the substrate as shown in Fig. 2a. The cleaning pretreatment yielded a rough surface that was ideal for the subsequent coatings. Figure 2b shows the SEM image of the Ti/IrO₂-SnO₂-Sb₂O₅ electrode. It was only used for carrying out some comparative EO experiments, but it is interesting to realize that high-quality anodes were obtained. As observed, the Ti surface was perfectly coated, unlike DSA prepared by thermal

decomposition that typically exhibit broad cracks. The image depicts a slightly rough surface with particles of IrO₂-SnO₂-Sb₂O₅ between 1 and 5 μm in height, being uniformly distributed and giving rise to an average thickness of the coating of approximately 2 μm. Although impossible to distinguish, some small gaps are present between the particles, thus revealing the underlying Ti substrate, as confirmed by the EDX analysis. The distribution of the elements (Ir, Sn, and Sb) present on the surface was homogeneous, and results from EDX showed an atomic proportion of 18.1, 13.7, and 0.07 % for Ir, Sn, and Sb, respectively, while the Ti from substrate represented 43.1 %.

The appearance of the Ti/IrO₂-Ta₂O₅ electrode can be observed in Fig. 2c. The electrocatalytic activity of these IrO₂-based DSA electrodes is not only determined by the amount of Ir, but also by the morphology and crystalline structure. Again, the mud-cracked surface that is obtained upon thermal decomposition is avoided thanks to the milder manufacturing process. A good coverage results from PPM, with a uniform coating formed by ordered flakes with a grain size of about 5 μm. The presence of Ti, Ir, and Ta was confirmed by the EDX analysis.

Fig. 2 SEM images (*left*) and EDX analysis (*right*) for **a** pretreated Ti substrate, **b** Ti/IrO₂-SnO₂-Sb₂O₅ electrode, and **c** Ti/IrO₂-Ta₂O₅ electrode



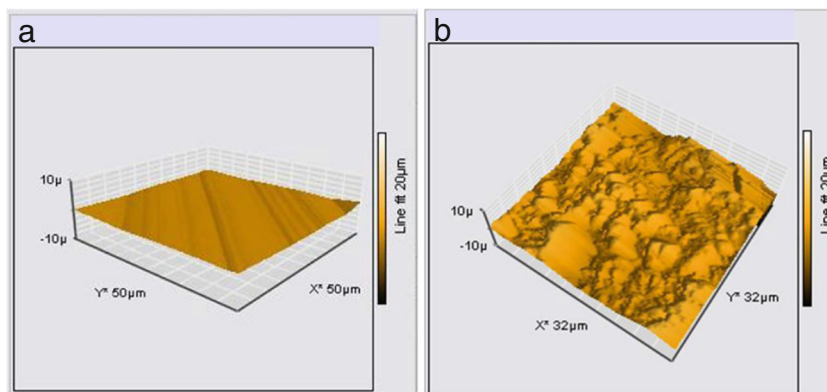
The actual profile of the Ti/IrO₂-Ta₂O₅ surface was further studied in detail by AFM. Figures 3a, b show the appearance of the bare, cleaned Ti and the DSA electrode, respectively. For the Ti substrate, the surface was smooth resulting in a very low roughness of 83 nm root mean square (rms). In contrast, a very rough surface with 612 nm rms can be seen for the DSA, which is related to the existence of evident oxide agglomerates exhibiting a certain diameter. The high surface roughness is very positive for upcoming electrochemical treatments since it is directly related to a larger surface area that automatically increases the number of electroactive sites and, therefore, enhances the electrocatalytic activity.

The ability of these rough DSA electrodes to produce ·OH was evaluated by two methods (see details in “[Electrolytic system for electro-oxidation](#)” and “[Instruments and analysis procedures](#)” sections). For spin trapping, 0.05 M Na₂SO₄ solutions in the absence (blank solution) or presence of 10 mM DMPO were treated by EO under different conditions of current and pH. Figure 4a depicts a representative ESR spectrum obtained using the Ti/IrO₂-Ta₂O₅ electrode at 10 mA cm⁻² and pH 3.0. All ESR spectra were similar to that of the blank solution, that is to say, without the characteristic bands of the ·OH-DMPO adduct. This agrees with findings on IrO₂-based DSA using *N,N*-dimethyl-*p*-nitrosoaniline (RNO) as the spin trap (Panizza and Cerisola 2009). In contrast, Fig. 4b allows observing the spectrum obtained using Fenton’s reaction, where a 0.05-M Na₂SO₄ solution at pH 3.0 with H₂SO₄ and containing 10 mM DMPO, 1 mM H₂O₂, and 0.1 mM Fe²⁺ was allowed to react for 10 min. The four characteristic bands revealing the presence of the adduct can be clearly seen. Considering that ESR is able to detect concentrations as low as 1 × 10⁻⁸ M of hydroxyl radical, it can be hypothesized that either the amount of ·OH formed at the Ti/IrO₂-Ta₂O₅ surface is below such threshold or this radical is quite chemisorbed on the surface. Another indirect technique was then employed in order to confirm or refute these results. EO of 0.05 M Na₂SO₄ solutions was carried out potentiostatically at various anodic potentials between +1.0 and +2.0 vs Ag|AgCl (3.5 M KCl). The presence or absence of

the Ti(IV)-H₂O₂ complex was evaluated by UV/Vis spectrophotometry. No signal was detected at 408 nm, thus confirming that the ·OH concentration is so low that no measurable H₂O₂ was produced by dimerization. In contrast, H₂O₂ was detected in trials with the Ti/IrO₂-SnO₂-Sb₂O₅ anode at potentials between +1.5 and +1.9 V. This informs about the nature of the ·OH radicals formed on SnO₂, which are partially physisorbed, i.e., more loosely adsorbed than those formed on IrO₂-based DSA.

The electrochemical characterization of the Ti/IrO₂-Ta₂O₅ electrode was performed in media made with 0.05 M Na₂SO₄, 0.05 M NaCl or mixtures of 0.025 M Na₂SO₄+0.025 M NaCl at pH 3.0 or 8.0 in order to simulate different typical conditions at the dairy, in the absence or presence of 5 mM indole as a representative of the organic pollutants contained in the wastewater of interest. The different background electrolytes did not exert great effects on the electrochemical responses and thus, only the CV results obtained in Na₂SO₄ are presented in Fig. 5a. Cyclic voltammograms were recorded between +0.2 and +1.2 V, corresponding to the stability region before hydrogen and oxygen evolution at 50 mV s⁻¹. The appearance of redox peaks between 0.6 and 0.8 V can be usually related to the redox transition of oxygen iridium group species Ir(III)/Ir(IV) and/or Ir(V)/Ir(IV), which is typical for IrO₂-based DSA (Xu et al. 2009). However, such response can be hidden for relatively low percentages of Ir (Li et al. 2006). This is the case for the present anode, as shown in Fig. 5a. A pseudocapacitive region arises due to charging of the electrical double layer, whereas the onset of the oxygen evolution reaction (OER) begins at more positive potentials, as explained below. The presence of indole simply led to a lower anodic and cathodic capacitance, probably due to the adsorption of the organic molecules on the surface. No faradaic processes were associated to it in this potential range, indicating that the molecule oxidation will only occur, if it turns out to be electrochemically active, at the same potentials as or higher than the OER. Next, linear sweep voltammograms were recorded between +0.6 and +1.6–1.8 V at 5 mV s⁻¹ after cycling the potential forward and backward several times in

Fig. 3 AFM images of **a** pretreated Ti substrate and **b** Ti/IrO₂-Ta₂O₅ electrode



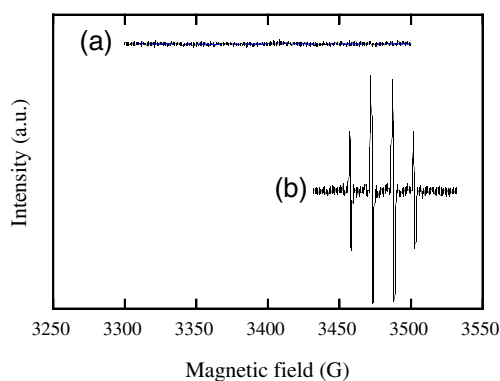


Fig. 4 Analysis of the $\cdot\text{OH}$ -DMPO adduct from the ESR spectra obtained **a** after 10 min of electro-oxidation of 10 mM DMPO solution in 0.05 M Na_2SO_4 medium at pH 3.0 using a $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ electrode at 10 mA cm^{-2} and **b** in Fenton's reaction

order to ensure that the voltammogram was recorded under quasistationary conditions. As in the previous case, the behavior in Na_2SO_4 medium at pH 3.0 shown in Fig. 5b was representative for the other media as well. In the absence of indole, the O_2 evolution started at about 1.32 V vs Ag/AgCl (3.5 M KCl), which agrees with tabulated values for IrO_2 -based DSA (Panizza and Cerisola 2009). This potential is +0.29 V more positive than the predicted thermodynamic potential of 1.23 V vs SHE in acid media, which allows classifying it as an anode with a low O_2 evolution overpotential, but

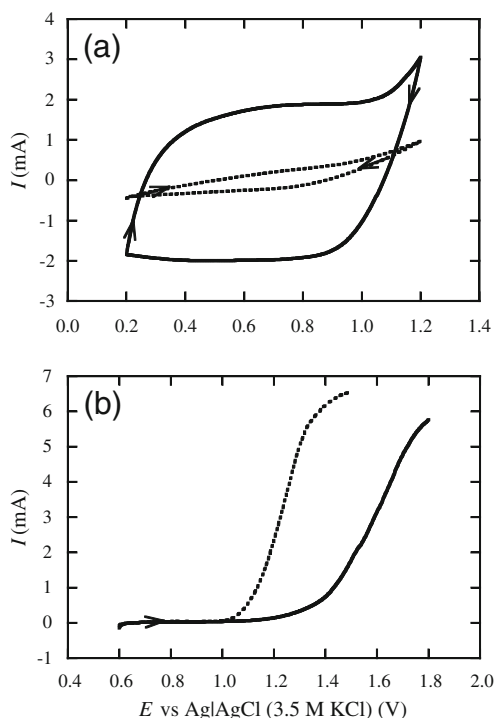


Fig. 5 Electrochemical characterization of the $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ electrode in 0.05 M Na_2SO_4 in the absence (*solid lines*) or presence (*dashed lines*) of 5 mM indole at pH 3.0. **a** Cyclic voltammograms recorded at 50 mV s^{-1} between +0.2 and +1.2 V. **b** Linear sweep voltammograms obtained at 5 mV s^{-1} between +0.6 and +1.6–1.8 V

still favoring the $\cdot\text{OH}$ -mediated oxidation of organic pollutants (Panizza and Cerisola 2009). As can be observed in Fig. 5b, the polarization curves shifted to less positive potentials in the presence of indole. The H_2O discharge took place earlier and current intensity increased for a fixed value of the potential. This experimental evidence suggests the direct oxidation of the organic compound within the region of O_2 evolution, which agrees with findings reported for the direct oxidation of oxalic acid at $\text{IrO}_2\text{-Ta}_2\text{O}_5$ (Scialdone et al. 2009). Similarly, Keech et al. (2002) reported that indole undergoes direct electron transfer at Pt anodes.

Electro-oxidation: testing of $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ electrodes with solutions of indole

The performance of the $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ anode in EO experiments was investigated with solutions of 100 mL containing 1 mM indole (100 mg L^{-1} TOC). The influence of the background electrolyte, applied current, and pH value is highlighted in Fig. 6 via the TOC evolution with electrolysis time. Figure 6a depicts the TOC decay for solutions containing 0.025 M $\text{Na}_2\text{SO}_4 + 0.025 \text{ M NaCl}$. The effect of applied current was examined for 10, 100, and 200 mA at pH 8.0, which simulates the pH of the natural wastewater (Table 1). While TOC remained almost unchanged at 10 mA, the solution was slowly mineralized at 100 mA, with a maximum TOC removal of 30 % that was kept quite constant after 180 min. In contrast, the application of 200 mA led to a quicker, progressive TOC abatement, yielding the best results with 60 % mineralization at 360 min. This is partly due to the higher production of $\cdot\text{OH}$ and the enhanced direct oxidation at the higher anode potential. Anyway, it is evident that a system based on EO alone using a $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ electrode could not compete with alternative processes, which reinforces the proposal of a combined electrochemical treatment. The EO of oxalic acid has also been reported to proceed very slowly with this kind of DSA (Martínez-Huitle et al. 2004). As observed in Fig. 6a, EO at 200 mA and pH 3.0 instead of 8.0 almost yielded the same TOC removal rate. Thereafter, the electrolyses were then performed at pH 8.0, having in mind that this would prevent from pH adjustment when treating the wastewater.

Figure 6b depicts the effect of the reaction medium at 200 mA and pH 8.0. Compared to the mixed electrolyte, the mineralization was slower in 0.05 M Na_2SO_4 , only reaching 25 % TOC abatement, whereas it was much quicker in 0.05 M NaCl , attaining almost 80 % at 360 min. The presence of Cl^- was then essential, thereby highlighting the predominant role of oxidation mediated by chlorinated species over the $\cdot\text{OH}$ -mediated oxidation. This is more clearly emphasized by the poor concentration of strongly adsorbed $\cdot\text{OH}$ mentioned above at this IrO_2 -based DSA. In chloride media, the anodic discharge of anions plausibly led to the formation of Cl_2 and HClO/ClO^- (Comninellis and Nerini 1995; Martínez-Huitle

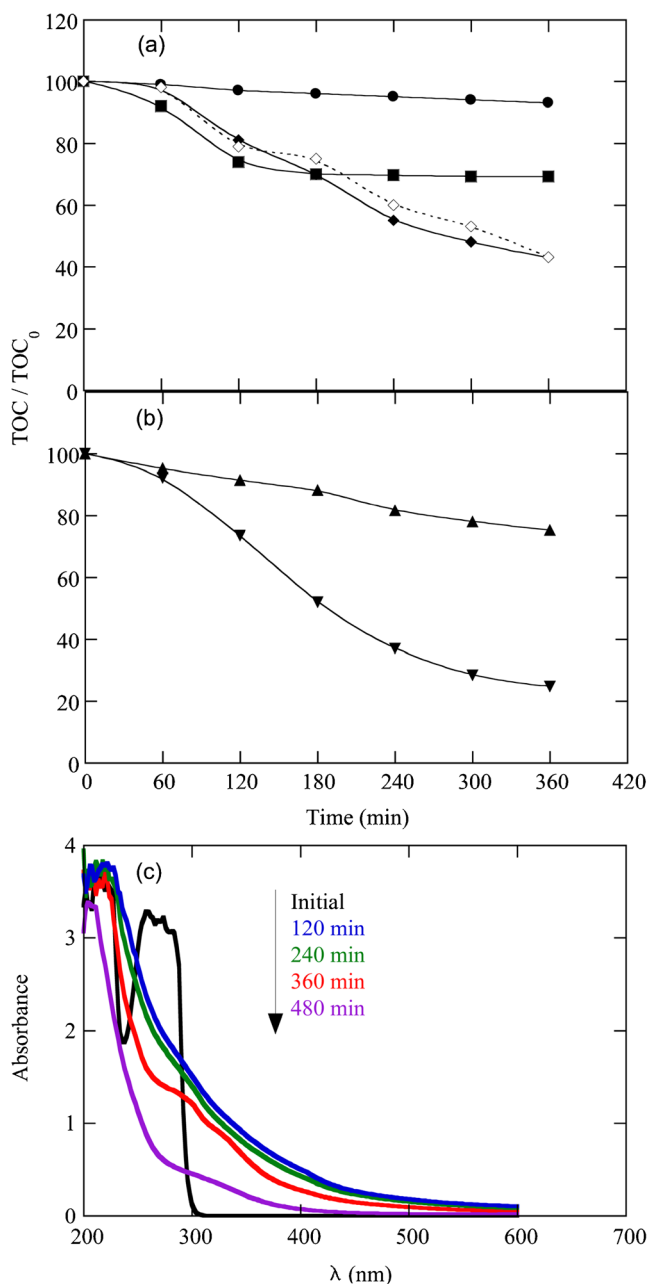


Fig. 6 a, b Normalized TOC removal with electrolysis time for the electro-oxidation of 100 mL of 1 mM indole using a Ti/IrO₂-Ta₂O₅ anode. In a, the solution contained 0.025 M SO₄²⁻+0.025 M Cl⁻ and electrolyses were made at 10 mA (filled circle), 100 mA (filled square), and 200 mA (filled diamond) at pH 8.0 and at 200 mA (white diamond) at pH 3.0. In plot b, the treatment was performed at pH 8.0 and 200 mA using 0.05 M SO₄²⁻ (filled triangle) or 0.05 M Cl⁻ (black down-pointing triangle). c Change in the UV/Vis spectra with time for the electro-oxidation of 1 mM indole in 0.05 M Cl⁻ at pH 8.0 and 200 mA

and Brillas 2008), which was evidenced by their characteristic odor identified during the electrolyses. Such mixture of agents is able to partially oxidize some organic molecules like indole and/or its reaction by-products. Cominellis and Nerini (1995) also showed that the addition of 85 mM NaCl catalyzed the oxidation of phenol using Ti/IrO₂ anodes due to the

participation of ClO⁻. The solutions containing chloride turned white, then dark and pale coffee in color, with a certain amount of foam, and, finally, the solution became almost colorless. Note that, in the previous EC step, NaCl was added for increasing the solution conductivity; the positive contribution of Cl⁻ now shown in EO opens the door to a beneficial sequential EC/EO treatment.

The time course of the solution absorbance was assessed for EO under the best conditions, i.e., in 0.05 M NaCl, as shown in Fig. 6c. At time 0, a clear absorption band appeared at about 280 nm, corresponding to the aromatic structure of indole. The band had already disappeared after 120 min of electrolysis, thanks to the action of ·OH and mainly to reactive chlorine species and the total remaining absorbance then derived from the formed by-products. Over time, the absorbance decreased because of the progressive removal of the intermediates, and a very low value was obtained at 480 min as expected from the low solution TOC achieved in this medium (Fig. 6b). On the contrary, the UV/Vis spectra in sulfate medium (not shown) remained practically unchanged, which agrees with the poor TOC removal shown in Fig. 6b.

Electro-oxidation: application to EC-pretreated dairy wastewater

Once the two individual processes were studied, the performance of the sequential treatment was assessed by using the best conditions previously established. Results of Table 1 gave evidence on the fact that the EC process applied at 9.09 mA cm⁻² for 120 min allowed to decrease the TOC from 1,062 to 198 mg L⁻¹. Samples of 100 mL taken from the resulting electrocoagulated water were then treated by EO with a Ti/IrO₂-Ta₂O₅ anode. The area was 6.6 cm² instead of 2.5 cm² in order to favor the mass transport of Cl⁻ (890 mg L⁻¹, ca. 0.025 M) towards the anode, based on the important role of that mediated process. The electrolyses were performed at a constant current of 200 mA and at the natural

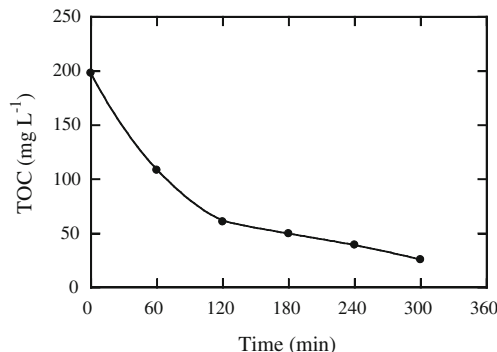


Fig. 7 TOC abatement with time for the electro-oxidation with a Ti/IrO₂-Ta₂O₅ anode of dairy wastewater pretreated by EC at 9.09 mA cm⁻². The solution of 100 mL contained 0.025 M Cl⁻ at pH ~8.0 and was electrolyzed at 200 mA

pH of about 8.0. During the treatment, a large amount of foam was formed onto the liquid and an intense odor of Cl_2 could be easily identified, becoming more intense with time. The trend of TOC over time is represented in Fig. 7. The mineralization rate was higher during the first 120 min with 72 % TOC decay. Afterwards, the decrease was less pronounced, but $<30 \text{ mg L}^{-1}$ TOC remained in the solution at 300 min. The good performance of the sequential electrochemical treatment has then been demonstrated and, therefore, a more detailed study will allow the optimization of all the parameters to propose the most convenient conditions for the in situ conditioning of the dairy wastewater. It is worth commenting that the integration of EC and EO has been recently reported for the treatment of carwash wastewaters, employing a BDD anode instead of much cheaper DSA (Panizza and Cerisola 2010).

Conclusions

This work has addressed several topics in order to assess the ability of a sequential electrochemical treatment for the remediation of a dairy wastewater:

1. Based on the wastewater characterization, the effluent from this dairy, which is conveyed to a reservoir of 12.5 m^3 had a very high organic matter content according to the Mexican legislation. Indole derivatives were important constituents of the wastewater.
2. EC with Al anode works successfully as a primary electrochemical method for separating colloids and ionic species from wastewaters such as those generated in cow sheds and the dairy industry, as revealed by the large percentages of removal of turbidity, COD, and TOC determined. Since the coagulation and sedimentation kinetics controls the efficacy of the process, the incorporation of a conical section at the bottom of the cell and the reduction of the electrode separation would probably enhance the process.
3. Two kinds of DSA anodes have been prepared by the Pechini method. They exhibited a high roughness, involving a large surface area for the OER. No signals corresponding to the $\cdot\text{OH}$ -DMPO adduct from the Ti/IrO₂-Ta₂O₅ anode were observed in the ESR spectra, which informs about the strong interaction of $\cdot\text{OH}$ with the anode surface, being somewhat weaker in the Ti/IrO₂-SnO₂-Sb₂O₅ anode.
4. The EO of indole solutions using the Ti/IrO₂-Ta₂O₅ DSA showed that chloride medium favors the degradation of the organic matter, which can be explained by the mediation of Cl_2 , HClO, and/or ClO^- formed on site. For this anode, this mechanism prevails over the action of $\cdot\text{OH}$.
5. The EO of EC-pretreated wastewater allowed a decrease from 198 to $<30 \text{ mg L}^{-1}$ TOC. This means that up to

98 % of initial TOC was removed via the combined EC/EO treatment, being much more effective than the individual processes.

Acknowledgments Support from CONACYT (Mexico) under program “Becas Mixtas 2012–2013 Movilidad en el extranjero”, as well as from MICINN (Spain) under project CTQ2010-16164/BQU, co-financed with FEDER funds, is acknowledged. The authors also thank the Centro de Graduados e Investigación en Química del Instituto Tecnológico de Tijuana.

Conflict of interest The author(s) confirm that this article content has no conflicts of interest.

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