Synthetic Boron-Doped Diamond Electrodes for Electrochemical Water Treatment

Electrodos de Diamante Dopado con Boro para el tratamiento electroquímico de aguas

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Abstract

Boron-doped diamond electrodes have emerged as anodic material due to their high physical, chemical and electrochemical stability. These characteristics make it particularly interesting for electrochemical wastewater treatments and especially due to its high overpotential for the Oxygen Evolution Reaction. Diamond electrodes present the maximum efficiency in pollutant removal in water, just limited by diffusion-controlled electrochemical kinetics. Results are presented for the elimination of benzoic acid and for the electrochemical treatment of synthetic tannery wastewater. The results indicate that diamond electrodes exhibit the best performance for the removal of total phenols, COD, TOC, and colour.

Resumen

Los electrodos de diamante dopados con boro han surgido como un nuevo material anódico debido a su propiedades como estabilidad física, química y electroquímica. Estas características hacen a estos electrodos especialmente interesantes para el tratamiento electroquímico de aguas residuales, debido sobre todo a su elevado sobrepotencial para la reacción de formación de oxígeno. Los electrodos de diamante presentan una eficiencia máxima para la eliminación de contaminantes en el agua, sólo limitada por la cinética del proceso electroquímico controlado por difusión. Se muestran algunos ejemplos como en la eliminación de ácido benzoico y en el tratamiento electroquímico de aguas sintéticas del curtido de pieles. Los resultados indican que los electrodos de diamante muestran el mejor rendimiento para la eliminación de fenoles, DQO, COT, y del color.

1. Introduction

Carbon materials have been widely used in both analytical and industrial electrochemistry from early in the 19th century [1]. These type of electrodes present several advantages: low cost, wide potential window, relatively inert electrochemistry, and electrocatalytic activity for a variety of redox reactions. The electrochemical applications of carbon electrodes are well known: metal production, energy storage in batteries and supercapacitors, and catalyst supports. The classical materials for electrochemical application are graphite, glassy carbon, and carbon black, and some extensive reviews can be found in the literature [2, 3].

Newer carbon-based material with outstanding electrochemical properties is diamond electrodes. Completely sp^3 hybridized, tetrahedral bonding of diamond produces materials with high hardness and low electrical conductivity. Crystalline diamond is a wide bandgap semiconductor, with a gap higher than 6 eV in a single crystal, and therefore an electrical insulator. However, the introduction of dopant atoms in the structure (usually boron or nitrogen) induces electrical conductivity.

2. Diamond electrodes: Synthesis and characterization

The first publication on conductive diamond is due to Pleskov et al. in 1987 [4]. Since then, there have been a large number of publications on this field. Some reviews collect the results obtained in applying these electrodes to various fields of electroanalysis, photoelectrochemistry, electrocatalysis, etc. [2]

Diamond electrodes are usually obtained by hot filament assisted chemical vapor deposition (HF-CVD) on a support heated to about 800-850 ºC. Silicon is the most suitable support, but diamond has been grown on metals such as W, Mo , Ti , Nb, etc. The precursor gas is usually a mixture of a volatile organic compound (methane, acetone, methanol, etc.) and hydrogen.

The most widely used dopant is boron, conferring a p-type semi-conducting character to diamond. The boron source can be a volatile compound introduced into the reactant gases, such as trimethyl borate or B_2H_6, or solid boron located near the substrate during growth of the diamond film. The boron doping level is often in the range of 10^{18}-10^{20} atoms/cm^3 or a B/C ratio of about 10^{-5} to 10^{-3}. Boron doped diamond (BDD) has randomly oriented microcrystallites with facets and grain boundaries characteristic of a polycrystalline material.

Figure 1a shows a micrograph obtained with scanning electron microscopy of a Si/BDD electrode showing the typical morphology of these polycrystalline diamond electrodes. Depending on the preparation procedure, the crystallite size may vary between 0.2 and 40 μm approximately.

Polycrystalline diamond films prepared in these conditions contain small amounts of sp^2 carbon usually located in the grain boundaries, as verified by Raman spectroscopy [5]. Diamond electrodes exhibit a 1332 cm^{-1} phonon band. The line width of this band and changes in smaller features of the diamond Raman spectrum are indicators of crystallinity and purity of diamond films [6].

This diamond band is used extensively to evaluate the relative amounts of sp^3 and sp^2 hybridized carbon in diamond electrodes. The 1360 cm^{-1} intensity relative to the 1332 cm^{-1} band is a sensitive indicator of sp^2 impurities in natural or synthetic diamond, since Raman cross section for sp^2 carbon is approximately 50 times that of sp^3 carbon. Boron doping at the high levels results in observable changes in the symmetry of the 1332 cm^{-1} Raman band, which can be used to determine the doping level [7].
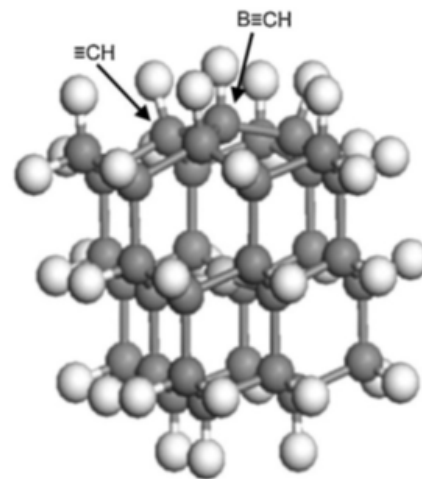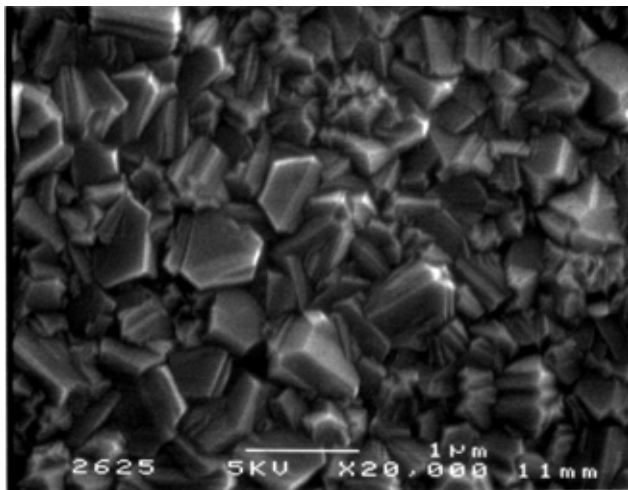
Figure 1. a) SEM images of a BDD film deposited on a silicon wafer. b) Simulated structure of a BDD. Hydrogen (white)-terminated diamond structure containing carbon and boron atoms.

Figura 1. a) Imágenes SEM de un depósito de BDD sobre Si, b) estructura simulada de BDD. Estructura de diamante conteniendo átomos de carbono, boro e hidrógeno (blancos).

3. Electrochemistry of diamond electrodes

BDD electrodes shows greater chemical stability compared with common sp^2 hybridized carbon electrode materials (i.e., graphite and glassy carbon electrodes). In addition to a long lifetime, the low chemical reactivity results in a wider electrochemical potential window.

Figure 2 shows cyclic voltammograms of a BDD electrode immersed in an aqueous solution, containing perchloric acid as supporting electrolyte.

In the high-scale potential range (figure 2, top), BDD electrode has a very wide electrochemical stability window that reach up to +2.5V at positive potentials. Above that potential the Oxygen Evolution Reaction (OER) takes place. This very high overpotential

for OER makes this electrode very suitable for electrochemical degradation of organic compound, and also for electroanalysis.

Figure 2, bottom, shows the comparison between a BDD electrode and a graphite electrode. It can be observed that the BDD electrode is characterized by a low current density in the double layer charge, if compared to the capacitive current obtained with graphite electrode. The oxidation process observed at 1.9V has been related to the reactivity of non-diamond carbon species (sp^2 carbon) or impurity situated in the grain boundaries of the diamond surface. Undoped diamond has no electronic states within its band gap, which covers most of the electrochemical potential scale. Boron doping introduces "midgap" states that increase conductivity and electron transfer rates. In
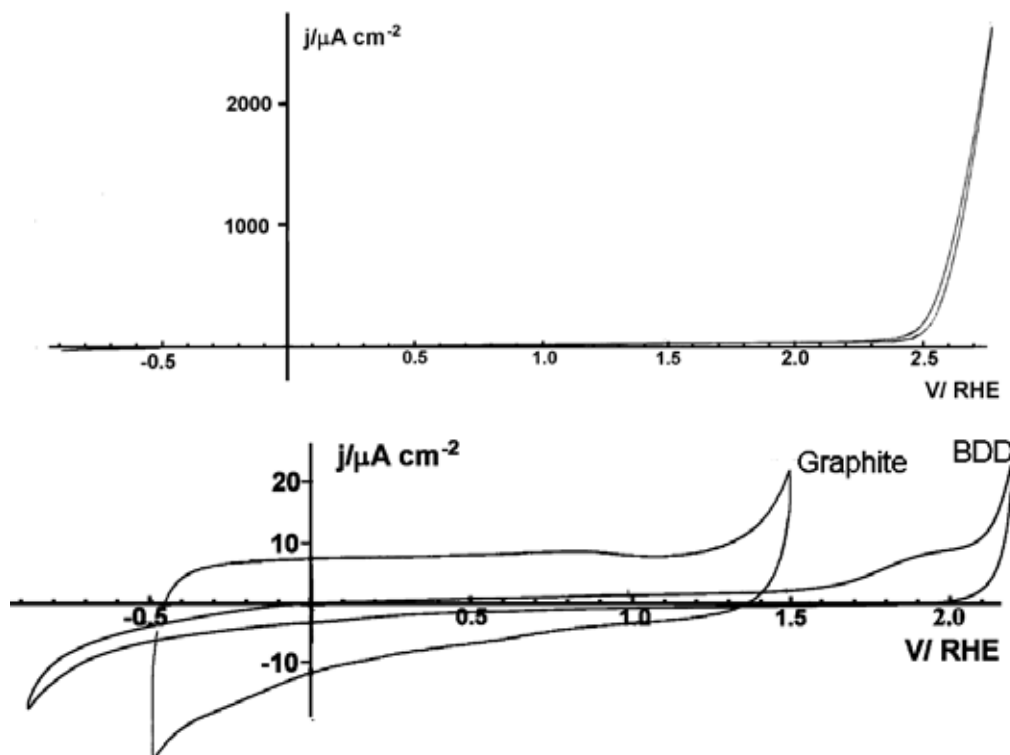

Figure 2. Cyclic voltammograms in aqueous 0.1M perchloric acid solution of a BDD diamond electrode (figure on top) and comparison between a BDD electrode and a graphite electrode (figure on bottom).

Figure 2. Voltagramas cíclicos de un electrodo BDD en ácido perclórico 0.1M (figura de arriba) y comparación entre un electrodo de BDD y un electrodo de grafito (figura de abajo).

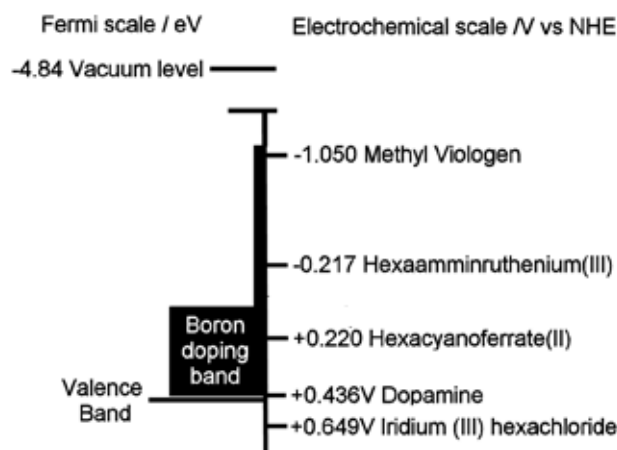that manner BDD is able to transfer electrons to most of the common redox probes, as showed in figure 3.

Figure 3. Energy states in BDD compared with the redox potentials of usual redox probes.

Figura 3. Estados energéticos del BDD comparados con los potenciales redox de diferentes pares redox.

The electrochemistry of organic compounds on BDD electrodes depends on the nature of surface adsorption. Standard redox probes have been studied on BDD electrodes in order to check the intrinsic electrocatalytic activity of this surface. As indicated by McCreery diamond electrodes has not adsorption sites and present a low electron transfer rate for redox as dopamine that requires adsorption, while methyl viologen voltammogram on BDD is quite similar to that on GC, since that compound can be considered as outer-sphere probe [2].

The intrinsic electrocatalytic activity of diamond, due to its lack of adsorption sites is low, but due to its inertness and low background currents this electrode is particularly interesting for fundamental studies on the electroactive compounds. The boron doped diamond electrode (BDD) is a suitable support for the characterization of electrocatalyst due to its high chemical and electrochemical stability, low background current, large electrochemical window and high thermal stability [8, 9].

## 4. Diamond electrodes, ideal anodes for electrochemical wastewater treatments

One of the most suitable treatments which can be performed on an effluent containing highly pollutants is the direct anodic oxidation (the so-called electrochemical incineration). In this process the electrode material must have a high efficiency of organic compounds oxidation, as well as a good stability under anodic polarization. A suitable model for understanding the processes of oxidation of organic compounds should also take into account the competitive reaction which occurs during the anodic oxidation of the organic compound, which is the Oxygen Evolution Reaction (OER).

The mechanism of electrochemical production of oxygen in aqueous media has been widely studied and different mechanisms have been proposed. There is a common initial step: a one-electron transfer to the solvent and the generation of an OH• radical in an active site surface electrode:

$$A_{(s)} + H_2O_{(l)} \rightarrow A_{(s)}(OH\bullet_{(ads)}) + H^+_{(aq)} + e^-_{(s)}$$
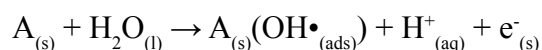
Being *A* the active site of the electrode. The following

steps of the mechanism depends on the nature of the electrode used, concretely on its affinity for the OH• formed. At this point we can identify two types of mechanism, depending on whether the oxygen species is weakly adsorbed (physisorbed) or strongly adsorbed (chemisorbed) on the electrode. If the hydroxyl radical is physisorbed, the OH• is released to the solution where forms oxygen:

$$OH\bullet_{(aq)} \rightarrow O_{2(g)} + 2H^+_{(aq)} + 2e^-_{(s)}$$
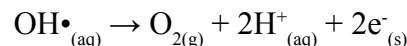
A reaction intermediate of this step is the formation of a peroxide radical ($O_2\bullet$) and it requires an important accumulation of physisorbed hydroxyl radicals and takes place at the potential of the H_2O/H_2O_2 redox couple (+1.77V/NHE). The production of oxygen by this route is not influenced by the chemical nature of the surface of the electrodes, because the chemical state of the electrode is not modified by the electron transfer reaction, but provides a physical adsorption site for the OH• radical. These electrodes are called "non-active" electrodes. This behavior is typical of electrode materials with absence of electroactive sites in the range of potentials between the thermodynamic potential for oxygen production (+1.23V/NHE) and the potential of H_2O/H_2O_2 redox couple, i.e. metal oxides in the highest oxidation state (such as PbO_2 or SnO_2). BDD electrode presents no redox active sites in that range of potentials and can be classified as non-active electrode (see figure 2).

These non-active electrodes present high overpotentials for the OER and therefore they are suitable electrodes for electrochemical oxidation-incineration of organic pollutants in industrial wastewaters, being the next reaction the final oxidation of a generic organic compound (R):

$$OH\bullet_{(aq)} + R_{(aq)} \rightarrow xCO_2 + yH_2O + H^+ + e^-$$

This reaction takes place at high overpotential, and the generation of OH• at high concentration favors the selective oxidation of organic, to give mainly CO_2. This electrode is also suitable for the electrochemical production of reactive oxidants such as ozone and hydrogen peroxide, because of their high OER overpotential. A model proposed by Comninellis et al. is useful for predicting the efficiency of electrochemical oxidation of organic compounds with "pure" non-active electrodes [10, 11]. It permits the prediction of the chemical oxygen demand (COD) and instantaneous current efficiency (ICE) during the electrochemical oxidation of organic pollutants on Si/BDD electrodes in a batch recirculation system under galvanostatic conditions.

The model supposes that the electrochemical oxidation-incineration of an organic compound is complete to CO_2, due to electrogenerated active intermediates formed by water discharge (OH radicals). The reaction between the OH radicals and the organic compound is considered much faster than the mass transport of the organic compound towards the anode.

Under these conditions, the limiting current density for the electrochemical incineration can be related to a global parameter of the solution, the Chemical Oxygen Demand (COD):
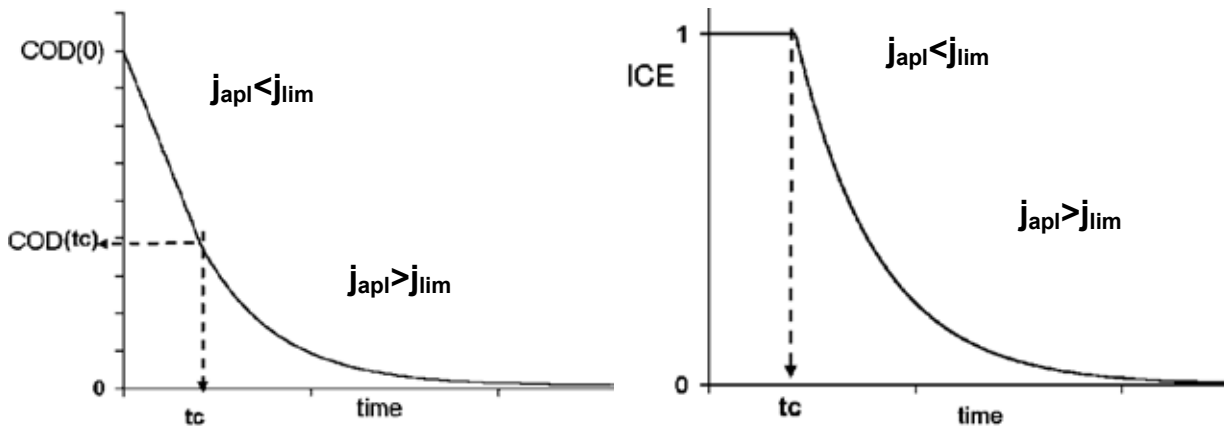
$$j_{lim}(t) = 4Fk_m COD(t)$$

Figure 4. Evolution of the Chemical Oxygen Demand (COD) and Instantaneous Current Efficiency (ICE) as a function of time predicted by the Comninellis model during the galvanostatic oxidation of organic compounds in aqueous solution.

Figura 4. Variación de la demanda química de oxígeno (COD) y eficiencia en corriente instantánea (ICE) con el tiempo de electrolisis según el modelo de Comninellis durante una oxidación galvanostática de compuestos orgánicos en disolución acuosa.

Where $j_{lim}(t)$ is the limiting current density (A m^{-2}) at a given time t, F is the Faraday constant (C mol^{-1}), k_m is the average mass transport coefficient in the electrochemical reactor (m s^{-1}) and COD(t) is the chemical oxygen demand in the electrolyte at a given time t. This equation is valid for the electrooxidation of any organics and even when the solution contains more than one compound.

Depending on the applied current density (j_{appl}), two different operating regimes are identified: (i) $j_{appl.} < j_{lim}$: the electrolysis is under current control, the current efficiency is 100% and COD decreases linearly with time; (ii) $j_{appl.} > j_{lim}$: the electrolysis is under mass transport control and secondary reactions (such as oxygen evolution) start, resulting in a decrease of ICE. In this last regime, COD removal due to mass-transport limitation follows an exponential trend. The equations that describe the temporal trends of COD and ICE in both regimes are summarized in Table 1 and the expected evolution with time of COD and ICE during the electrochemical oxidation during the electrolysis at constant current is shown in figure 4.

As example, Figure 5 shows the evolution with time of COD and ICE during the electrochemical oxidation of different solutions of benzoic acid at constant current. Electrolysis at high anodic potentials in the region of electrolyte decomposition causes complex oxidation reactions that lead to the quasi complete incineration of BA. There is no indication of electrode fouling. In the inset of Figure 5, the theoretical value of COD and current efficiency trends calculated from the model (Table 1) are reported with the electrical charge. As predicted from the model, at

the beginning of the electrolysis and at high benzoic acid concentration (8.86 mM, COD =2500 ppm), the reaction is under current limiting control ($j<j_{lim}$). This result in an instantaneous current efficiency (ICE) of almost 100% and in a linear decrease of COD with the specific charge passed. After some time of electrolysis, the COD in the solution decreased until a critical value, COD(t_C) is achieved after this value both ICE and COD decrease exponentially with the specific charge passed as predicted by the model [12].
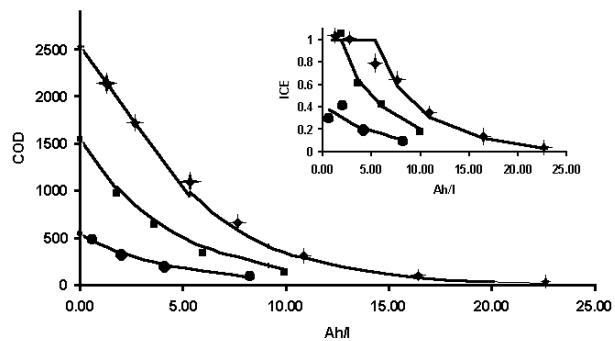

Figure 5. Evolution of COD and ICE (inset) during electrolysis of benzoic acid in 0.5M HClO$_4$. Initial concentration of benzoic acid, (✦) 8.86 mM, (■) 4.76 mM, (●) 2.11 mM. Anode: Boron-doped diamond electrode. Zr plate as cathode. T=25 °C. j= 24 mA cm^{-2}. The solid lines represent the model prediction.

Figura 5. Variación de la demanda química en oxígeno (COD) y la eficiencia en corriente instantánea (ICE)(figura insertada) en la oxidación de ácido benzoico en HClO$_4$ 0.5M , (✦) 8.86 mM, (■) 4.76 mM, (●) 2.11 mM. Ánodo: Electrodo de diamante dopado con boro. Cátodo: Zr. T=25 °C. j= 24 mA cm^{-2}. Las líneas sólidas correspondes a la simulación según el modelo.

Table 1. Equations that describe instantaneous current efficiency (ICE) and chemical oxygen demand (COD) during benzoic acid oxidation at Si/BDD electrode in acid solution.

Tabla 1. Ecuaciones que describen la eficiencia en corriente instantánea y la demanda química de oxígeno (COD) durante la oxidación de ácido benzoico con un electrodo Si/BDD en disolución ácida.

	Instantaneous current efficiency ICE	Chemical Oxygen Demand COD (molO$_2$ m^{-3})
under current control $j_{applied} < j_{limit}$	$ICE(t) = 1$	$COD(t) = COD(0)\left(1 - \dfrac{\alpha A k_m}{V_R}t\right)$
under mass transport control $j_{applied} > j_{limit}$	$ICE(t) = \exp\left(-\dfrac{A k_m}{V_R}t + \dfrac{1-\alpha}{\alpha}\right)$	$COD(t) = \alpha COD(0) * \exp\left(-\dfrac{A k_m}{V_R}t + \dfrac{1-\alpha}{\alpha}\right)$

Being $\alpha = j_{appl}/j_{lim(t=0)}$ and V_R the volume of the treated water
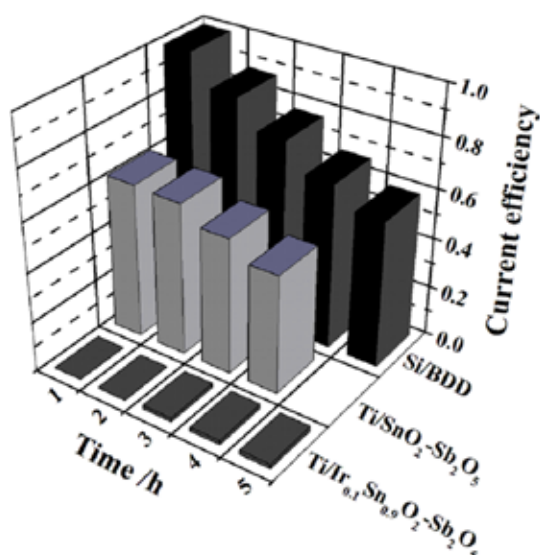
Figure 6. Current efficiency for the electrochemical incineration of tannery wastes with different anodes.

Figura 6. Eficiencia en corriente de la eliminación electroquímica de aguas sintéticas procedentes del curtido de pieles usando diferentes ánodos.

In similar manner, the electrochemical oxidation of other organic compounds on BDD anode demonstrates that the performance of this electrode is excellent, not only in the removal of pure refractory organic compounds [13], but also in complex mixtures of pollutants like in the electrochemical treatment of a synthetic tannery wastewater prepared with several compounds used by finishing tanneries. Results showed that faster removals of these parameters occurred when the Si/BDD was used as anode in comparison with other highly efficient anodes such as Ti/SnO_2Sb (see figure 6). This electrode was also the more efficient to remove the wastewater color [14].

Table 2 shows total organic carbon (TOC) removal and energy consumption after 4 h of electrochemical treatment of the synthetic tannery wastewater under different conditions. The Si/BDD anode is energetically more efficient than the other electrodes because it leads to faster TOC removal with lower energy consumption, although good results in terms of energy consumption are also obtained with the Ti/SnO_2–Sb anode. However, the latter anode has limited applicability because of its low stability. The increase in current density in the case of the Si/BDD anode results in faster wastewater mineralization with higher energy consumption.

Table 2. TOC removal and energy consumption obtained after 4 h of electrochemical treatment of the synthetic tannery wastewater in 0.10 mol L^{-1} Na_2SO_4.

Tabla 2. Eliminación de TOC y consumo energético obtenido tras 4 h de oxidación electroquímica de un agua sintética procedente del curtido de pieles en Na_2SO_4 0.1M.

Electrolysis condition	TOC removal (%)	Energy consumption per removed TOC (kWhg^{-1})
Ti/SnO_2–Sb–Ir, 25mAcm^{-2}	2.1	2.55
Ti/SnO_2–Sb, 25mAcm^{-2}	56.1	0.10
Si/BDD, 25mAcm^{-2}	79.1	0.08
Si/BDD, 100mAcm^{-2}	98.3	0.55

5. Conclusions

Electrochemical treatment of wastewaters have undergone rapid development due to the appearance of a new material: boron doped diamond films. These BDD electrodes are attractive as anodic material due to their high physical, chemical and electrochemical stability and mainly in the wastewater treatment, due to their high overpotential for water oxidation-reduction processes. These properties confirm these BDD materials as one of the most promising electrode material for the treatment of industrial pollutants in water.

The good agreement between the experimental data and the theoretical model indicates that these electrodes present the maximum efficiency in pollutant removal, just limited by diffusion-controlled electrochemical kinetics. In the case of benzoic acid on the reaction proceeds by electrogenerated intermediates (hydroxyl radicals) on BDD and it is a fast reaction. The electrochemical treatment of more complex systems (synthetic tannery wastewater) indicates that Si/BDD electrode exhibits the best performance for the removal of total phenols, COD, TOC, and colour.

6. References

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