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Electrochemical Oxidation of Diethyl Phthalate Using Boron Doped Diamond, Modified with Gold Particles

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In this work we show the results related to the electrochemical degradation of Diethyl phthalate using a boron doped diamond electrode modified with gold particles in a Na_2SO_4 electrolytic media with and without the presence of the chloride ion. Our results show that the presence of gold particles on the electrode increases the degradation efficiency in 10 %.

Keywords: Diethyl Phthalate, electrochemical degradation, Boron doped diamond electrode, gold particles

1. INTRODUCTION

The increment of the pollution of water and wastewater with some organic compounds is growing concern, because in some cases conventional biological wastewater treatments are no longer efficient enough in the removal of the toxic components present in water. Advanced Oxidation Processes (AOP), such as electrochemical mineralization, has been reported to be an efficient way to remove organic pollutants from wastewater [1-4], such as phthalic acid esters (PAEs) [5,6]. PAEs have been identified in wide and variety parts of the environment, such as groundwater, river water, drinking water, open ocean water, soil, lake and marine sediment [7].

Phthalic acid esters are used in diverse industries, mostly as a plasticizer. Particularly, diethyl phthalate (DEP) can be found in a wide variety of consumer products, such as plastic packaging films (e.g. toothbrushes, automotive components, tool handles), more than 50 cosmetic formulations (e.g. bath preparation, eye shadow, toilet waters, perfumes, hair sprays, wave sets, nail polish, detergents, aftershave lotions) and in medical treatment tubing, among others. Therefore, human exposure to DEP is expected to be significant [8]. Phthalic acid esters have been reported to be extremely and chronically toxic to freshwater and marine aquatic life by the US Environmental Protection Agency [9]. Diethyl phthalate has been reported to cause metabolic changes; more specifically it affects the activities of phosphatase and transaminases [10]. In long periods of exposure to lower concentrations of DEP in male Wistar rats causes increases the numbers of peroxisome proliferation causing an increase of the liver weights, also damages the metabolism of glycogen, cholesterol and triglyceride as well as altered liver histology [11].

The degradation of endocrine disrupters, as DEP, are mostly conduct by advance oxidation processes [12] and a combination of photocatalytic and sonolysis was described for DEP [13]. Electrochemical methods are widely used to study the incineration of endocrine disrupter, for example, for BPA a flow cell was used to study different variables such as flow rate, pH, and presence of chloride ion. The authors conclude that the presence of chloride ion improve the degradation rate at high flow rate and current density [14]. Degradation of Dimethyl Phthalate (DMP) is the most study where BDD is cited as the best anode to be used compared with platinum [6,15] or DSA^{TM} or PbO_2 [16,17] but the use of chloride ion in the electrolytic media is not discussed only by the formation of chlorinated intermediaries [18].

The modification of BDD with metal nanoparticles had been studied since a few years, trying to improve its performance in the detection of different molecules or to study the electrocatalysis of different reactions, such as, methanol oxidation [19]. The strategies of the modification in general are the electroreduction of $AuCl_4^-$ from aqueous solution obtaining gold particle decorated BDD, the size range from 50 nm to 1-2 um. One problem is the stability due to the low adhesion of the particles in the electrode surface. Swain et al has been synthesized platinum modified BDD electrodes a chemical vapor deposition, including the platinum during the diamond synthesis improving the stability of the particles [20]. So in this work, we study the electrodeposition of gold on BDD electrodes and the modified electrode was applied to the electrochemical degradation of diethyl-phthalate.

2. EXPERIMENTAL

*2.1. Reagen*ts

Diethyl Phthalate (99,5%) was from Sigma – Aldrich was prepared in water with a concentration of 100 ppm in an supporting electrolyte of Na_2SO_4 (50 mM, Merck) in the non-chloride medium, but in the chloride medium were 50 mMNa_2SO_4 + NaCl (50 mM). All solutions were prepared with deionized water (Millipore Milli – Q system).

2.2. Materials

The Si/BDD (with boron-doping content from about 8000 ppm, Adamant Technologies) with an area of 1 cm^2 was used in a conventional three electrode electrochemical cell as working electrode, Ag/AgCl was used as reference electrode and a platinum coil (10 cm^2) was used as counter electrode. The gold modified BDD electrode was prepared by electrolysis at -0,2 V in a 0.5 M H_2SO_4 (Merck) containing 20 mM of $AuCl_4^-$, prepared previously by oxidation of gold with aqua regia, until reach a 0.1 C of electrical charge using a CH Instruments 604 C potentiostat.

2.3. Electrochemical degradation of the DEP

All the electrolysis were undertaken in a 250 mL one compartment reactor; carried out galvanostatically with an potentiostat CH instrument model 1140 C applying 30 mA cm^2 of current density until obtaining a charge of 10.140 C using BDD and gold modified BDD as anode and 316 Stanley steel was used as cathode.

2.4. Analyses

The degradation was followed through the *COD* removals. All measurements were made at several times; 0, 30, 60, 90, 180 and 240 min, taken a portion of the electrolyzed solution and oxidized by digestion for 2h at 150°C in a vial (HACH) that contains H_2SO_4, $K_2Cr_2O_7$, Ag_2SO_4 and $HgSO_4$. The absorbance after the digestion was read in a HACH spectrophotometer (model DR/2010) at 420 nm.

The UV-Vis decays were undertaken at the same time as in the previous procedure, using 1 mL of the electrolyzed solution and diluting it with 1 mL of distilled water (milli – Q grade). The absorbance of the sample was registered in a Shimadzu spectrophotometer (model UV-1800) scanning it from 200 to 400 nm. HPLC measurements were also made in a Shimadzu model 20A, with 2 pumps LC-20AD, UV-Vis SPD-20AD at 274 nm, autoinjector SIL-20AD; controlled by CBM-20AD.Mobile phase was Acetonitrile:water (45:55) with 1 mL min^{-1} as a flow rate using a Phenomenex C-18 150mm x 4.60 mm column.

3. RESULTS AND DISCUSSION

Such as mentioned in literature, previous to the electrodeposit of gold, the electrode was treated with a cathodic electrolysis at 0,03 $mAcm^{-2}$ by 20 min in 0.05 M Na_2SO_4 electrolyte to obtain an hydrogenated surface over that the gold is electrodeposited in order to obtain better results in adhesion and stability of the particle deposited [19]. Figure 1 shows the voltammetric profile of a BDD electrode in not stirred 0.5 M H_2SO_4 electrolyte before and after the electrodeposition of gold by the potential step. From the figure (solid line) is possible to observe the typical current peaks of the gold oxide formation and the corresponding reduction, showing that after the potential step, gold was electrodeposited in the BDD surface. The morphological characterization was done by the SEM images; to evaluate the changes that take place over the BDD surfaces and it is shown in Figure 2.

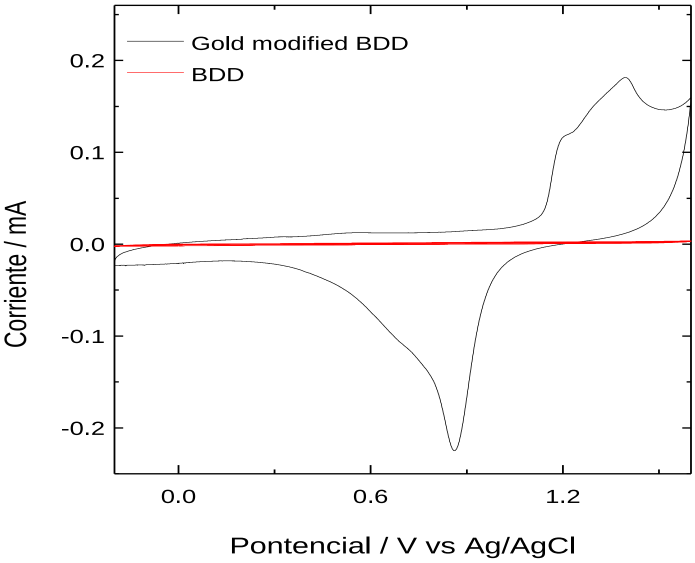


Figure 1. Voltammetric profile of a BDD electrode in 0.05 M H_2SO_4 at 0,1 V s^{-1}, before (red line) and after (black line) electrodeposited of gold particles in the BDD surface.

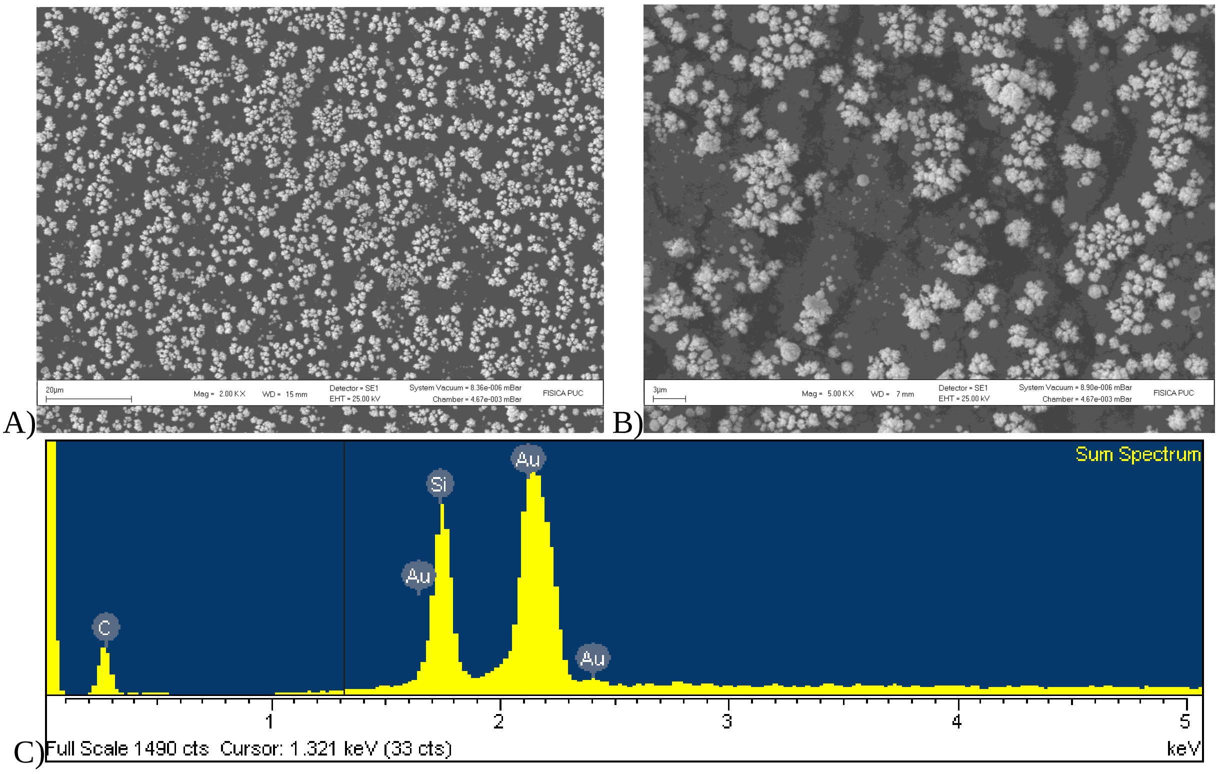
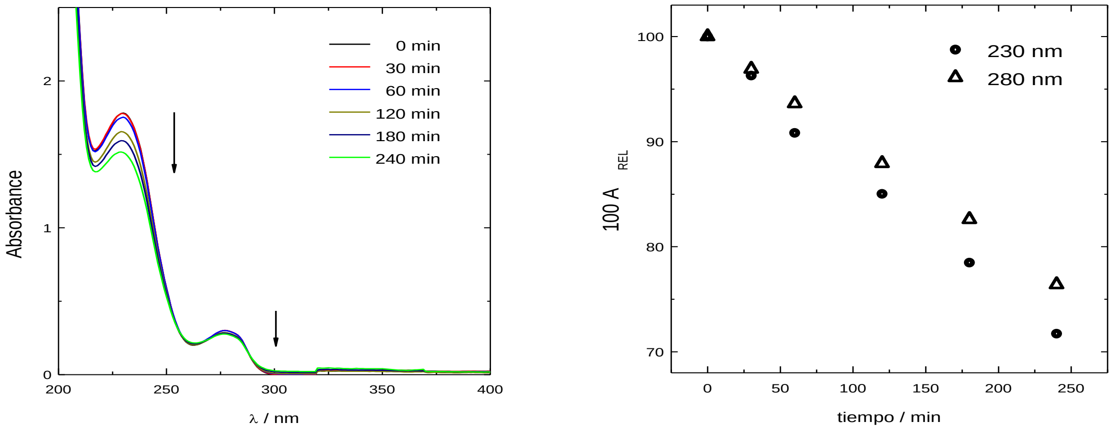


Figure 2. A) and 2 B) SEM images of the gold modified BDD electrode at different magnification. C) EDS analysis of the electrode surface obtained for the same sample.

Figure 2 A and B shows the SEM images of the gold modified BDD electrode at two magnification. In these figures is possible to observe a homogeneous distribution of particles over the electrode. The particles seem like cauliflowers indicating a progressive nucleation mechanism. The particle sizes varying between 100 nm to 3 μm, but the bigger ones are cumulus of smaller particles. Figure 2 C shows the EDS analysis indicating that the elements present in the electrode surface are Au, C and Si, corresponding to the gold particles and the BDD/Si used as substrate.

The BDD electrode and gold modified BDD electrode were used as anode in the electrolysis of diethyl phthalate (DEP) following the degradation of this compound by the UV-Vis spectra of the dissolution along the electrolysis. Figure 3 A shows the UV-Vis spectra of DEP at different times for the electrolysis of this compound using BDD anode. First, this figure shows that the DEP spectrum is composed by two bands centered at 230 nm and 280 nm, corresponding to the absorbance band of the phenyl and carboxylic radicals present in the [21]. In the same figure is possible to observe that along the electrolysis both signals decrease, indicating that the molecule are oxidized and degraded to other organic compounds and /or to CO_2.

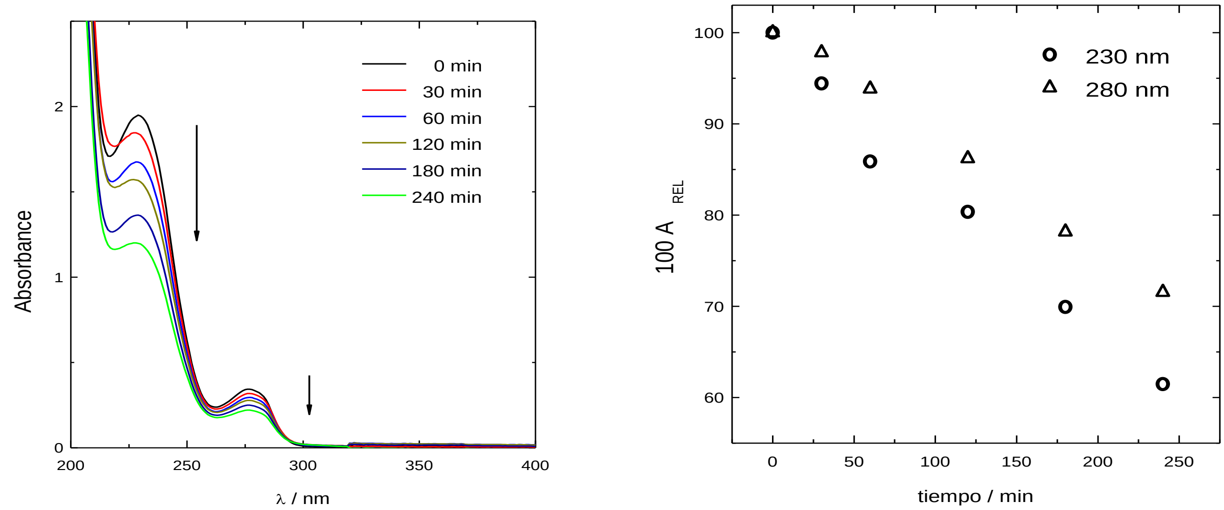


A) B)

Figure 3. A) UV-vis spectra of 100 ppm DEP in 0.05 M Na_2SO_4 electrolyte during the electrolysis using BDD anode at 0.0 mA cm^{-2}. B) relative absorbance decay for both absorption band (230 nm open circle, 280 nm open triangle) versus electrolysis time for data of figure 3 A.

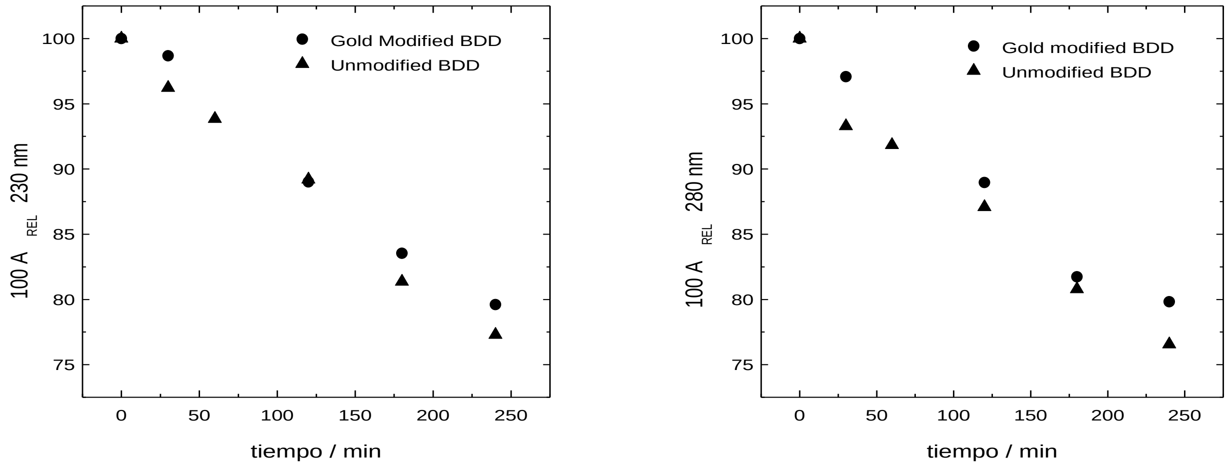
Figure 3 B shows the relative absorbance during the electrolysis for both signals, where is possible to observe that both signals decays until 70 % of the original value after 240 min of electrolysis. A slight difference between both signals is observed, but they are not significantly different to attribute a preferential attack by the hydroxyl radicals generated on the BDD surface.

Figure 4 A shows the decay in the absorbance of the signals of DEP during the electrolysis with the gold modified BDD electrode. In this figure a greater decay of the signals is observed, related to the effect of the presence of the gold particles in the electrode surface. Figure 4 B shows the relative absorbance decay versus time, where is possible to observe that they reach values between 60% and 70% of decay versus 70% and 75% with the unmodified electrode (figure 3 B). So the presence of this particles improve the degradation of DEP in a !0% approximately compared with the BDD anode without the gold particles.



A) B)

Figure 4. A) UV-vis spectra of 100 ppm DEP in 0.05 M Na_2SO_4 electrolyte during the electrolysis using gold modified BDD anode at 0.03 mA cm^{-2}. B) Relative absorbance decay for both absorption band (230 nm open circle, 280 nm open triangle) versus electrolysis time for data of figure 3 A.



A) **B)**

Figure 5. A) Relative absorbance decay for DEP electrolysis at 0,03 mA cm-2 using gold modified BDD electrodes (circles) and unmodified BDD electrodes (triangles) for absorption band centered at 230 nm B) same as figure 5 A, for absorption band centered at 280 nm.

It is well known that the presence of chloride ion in the electrolytic media improve the degradation of organic molecules due to the formation of different oxidant species depending of the pH of the media (HOCl, OCl^-, Cl_2), in our case the oxidant specie was HOCL due to the pH near 7.0 (pka

7.46). So, the same experiments were performed using electrolyte-containing chloride in the medium. Figure 5 shows the relative absorbance decay for both electrodes. From the figure is concluded that no difference is observed if the BDD is modified or not and the other fact observed is that the presence of chloride in the electrolytic media has no effect probably due to DEP is only oxidize by the hydroxyl radicals produced in the BDD surface and chloride ion compete with DEP for react with hydroxyl radicals.

Figure 6 shows the HPLC chromatograms of samples of the electrolyte obtained at the beginning of the electrolysis and after 240 min of degradation. In this figure is possible to observe that during the electrolysis the signal corresponding to the DEP is decreasing, such as showed by the COD and UV-Vis analysis, and after 240 min, start to appears a smaller signal at lower retention time, indicating the formation of more hydrophilic molecules during the degradation. This behavior was previously showed in the literature, so our data are in agreement with the previously reported degradation mechanism [3].

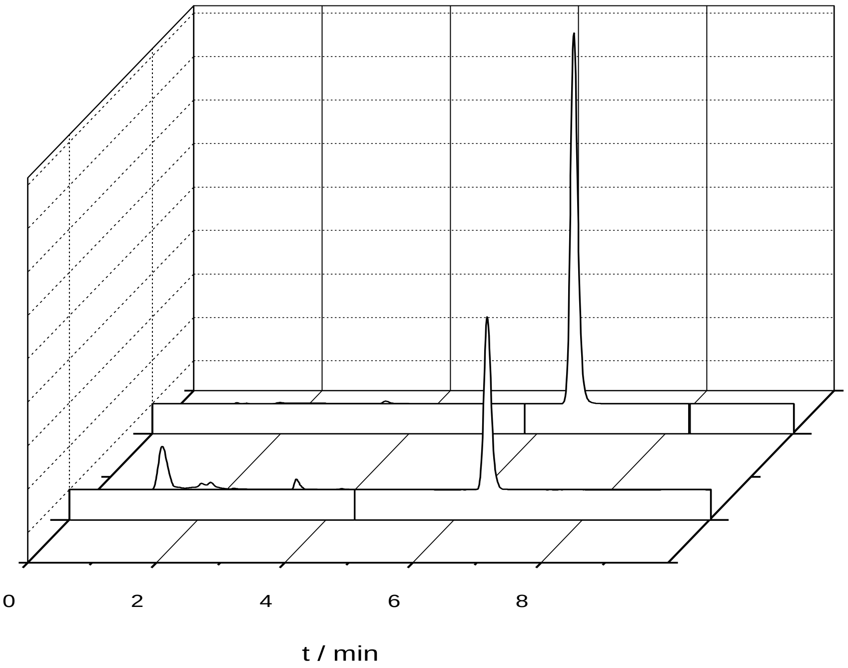


Figure 6. HPLC chromatographs obtained during the electrolysis of DEP using BDD anode in $Na_2SO_4$0.05 M, DEP 100 ppm, at t = 0 min and t = 240 min.

After degradation, the electrochemical response of the modified electrode was registered in 0.05 M H_2SO_4 where no potential peaks of gold were observe, attributed to the oxidation of gold to gold oxide. This problem with the stability is due to the high potentials reach during the electrolysis and need to be studied for further applications of this system or use different compounds to modificate the BDD electrode surface, such as metal oxides.

4. CONCLUSION

From this work is possible to conclude the following: Diethyl phthalate is degraded by electrochemical methods using BDD anode and the use of gold particles modified electrode increase the degradation efficiency in a 10 %. The presence of chloride ion in the electrolytic media has no effect. Finally the modification of BDD with metal particles could be a good strategy to improve the electrochemical degradation of organic compounds.

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