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CYCLIC VOLTAMMETRY TOOL FOR ASSESSING ELECTROCHEMICAL DEGRADATION OF DICLOFENAC

Monica Ihos[1,2], Florica Manea[2] and Rodica Pode[2]

[1]National R&D Institute for Industrial Ecology - ECOIND - Timisoara Branch, P-ta Regina Maria Nr.1, Et.2, 300004 Timisoara, Romania, e-mail: monica_ihos@yahoo.com
[2]"Politehnica" University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Bv. Vasile Pârvan Nr.6, 300223 Timisoara, Romania

ABSTRACT

The cyclic voltammetry (CV) experiments were carried out in order to assess the electrochemical degradation of diclofenac (DCF) at dimensionally stable anodes (DSA). The working electrode was a boron-doped diamond (BDD) electrode and electrolysed solutions of DCF in 0.1 M Na_2SO_4 supporting electrolyte were used. The electrolysed solutions were obtained previously in the electrochemical degradation of DCF at DSA electrodes, Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$, at various current densities and 120 minutes of electrolysis. The peak current abatement efficiency was calculated based on cyclic voltammograms (CVs) and the most efficient composition of DSA for DCF degradation was designated.

INTRODUCTION

The presence of pharmaceuticals in the environment rises concerning because of their ecotoxicity even at low levels of concentration, especially in aquatic environment [1-3]. Pharmaceuticals are not usually completely mineralized when they enter a wastewater treatment plant [4]. Concentration of many pharmaceuticals are barely reduced and they are, therefore, detected in wastewater treatment plant effluents. As a consequence it is necessary to develop technologies that remove efficiently the pharmaceuticals from wastewaters.
In the recent years the research of advanced oxidation processes has gained an increased interest, because these technologies have been shown to be able to oxidize efficiently most organic pollutants until mineralization to inorganic carbon [5,6]. Among advanced oxidation processes, the electrochemical advanced oxidation processes, and in particular, "anodic oxidation" and "electro-Fenton", have demonstrated good prospective at lab-scale level for the abatement of pollution caused by the presence of residual pharmaceuticals in waters [5].
The aim of this paper was to assess the electrochemical degradation of diclofenac (DCF), a non-steroidal anti-inflammatory drug, at dimensionally stable anodes (DSA) by using cyclic voltammetry (CV) to envisage the application of anodic oxidation to pharmaceuticals effluents treatment.

MATERIALS and METHODS

The CV experiments were performed by using an EcoChemie Autolab-PGSTAT 302 computer-controlled potentiostat-galvanostat and a Metrohm three electrode cell. A saturated calomel electrode (SCE) was used as reference electrode and a platinum plate of 1 cm^2 as a counter electrode. The working electrode was a BDD electrode with active surface area of

$0.071 cm^2$. The BDD electrode supplied by Windsor Scientific Ltd. was a mirror polished doped polycrystalline industrial diamond (microcrystalline and doping degree about 0.1% boron).

Prior to the electrochemical measurements, the working electrode was carefully cleaned, degreased and treated by polishing with alumina powder (0.1 mm), and finally washed with distilled water. The interface of the working electrode with the aqueous medium was stabilized by repeated cycling in solution of 0.1 M Na_2SO_4 supporting electrolyte in a potential range between -0.5 V and +1.5 V vs. SCE.

The CV experiments were carried out in initial solutions of DCF in 0.1 M Na_2SO_4 supporting electrolyte and electrolysed solutions resulted in the electrochemical degradation experiments of DCF at two DSA anodic compositions: Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$. The electrochemical degradation experiments were carried out prior to the CV ones and they are not presented here, only the working conditions are. The working conditions were: initial concentration of 10, 50, 100 and 200 mg/L DCF in 0.1 M Na_2SO_4 supporting electrolyte, applied current densities of 100, 200 and 300 A/m^2 and 120 minutes of electrolysis time.

The CV experiments were carried out at 50 mV·s^{-1} scan rates at room temperature.

Na_2SO_4 was analytical reagent grade from Merck, and DCF was used as received from Amoli Organics Ltd. All solutions were prepared with distilled water.

RESULTS

As it was found in our previous experiments [7] regarding the availability of BDD for DCF detection, the CVs of BDD electrode recorded in the presence of DCF exhibits peaks at about +0.7 V/SCE, suitable for detection purposes, and at about +1 V/SCE. These peaks could be also used for assessing the electrochemical degradation of DCF at DSA electrodes: Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$.
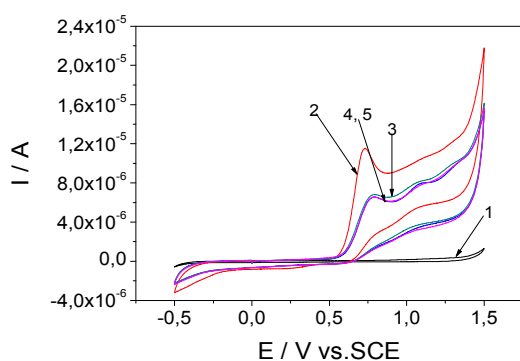

Fig. 1. **Cyclic voltammograms of BDD**
in 0.1 M Na_2SO_4 (1) and in presence of solutions from degradation of 200 mg/L DCF at
Ti/RuO_2-TiO_2 anodes : unelectrolysed (2) and after 120 min of electrolysis at 100 A/m^2 (3), 200 A/m^2 and 300 A/m^2 (4, 5); potential scan rate 0.05 V/s; potential range: -0.5 → +1.5 V/SCE

Fig. 2. **Cyclic voltammograms of BDD**
in 0.1 M Na_2SO_4 (1) and in presence of solutions from degradation of 200 mg/L DCF at $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ anodes : unelectrolysed (2) and after 120 min of electrolysis at 100 A/m^2 (3), 200 A/m^2 (4) and 300 A/m^2 (5); potential scan rate 0.05 V/s; potential range: -0.5 → +1.5 V/SCE
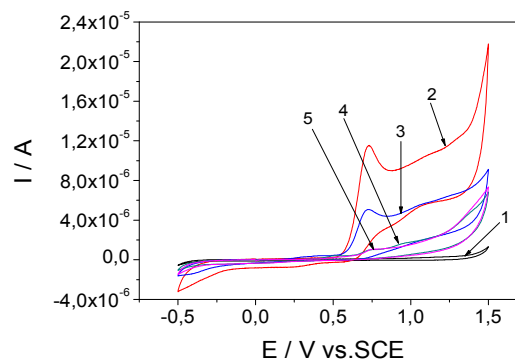
Figs. 1 and 2 shows the CVs of BDD recorded in the presence of initial unelectrolysed solutions of DCF and solutions from degradation of DCF at DSA electrodes. One can see that the CVs kept their shape along the abatement of the peak current at +0.7 V/SCE and

+1 V/SCE as the current density increased, that suggests the electrochemical degradation progress. The disappearance of current peaks in CVs (they are not presented in this paper), suggests a mineralization process along the degradation one.

Table 1. Peak current abatement efficiency in cyclic voltammetry experiments at BDD electrode carried out in electrolysed solutions resulted in the electrochemical degradation of DCF at Ti/RuO$_2$-TiO$_2$ anodes at various current densities and 120 min of electrolysis

DCF concentration of initial solution / mg/L	Current density / A/m^2	Peak current abatement efficiency at E = + 0.7 V/SCE / %	Peak current abatement efficiency at E = + 1 V/SCE / %
10	100	97.69	91.23
	200	100	96.69
	300	100	100
50	100	73.92	58.52
	200	90.39	79.82
	300	97.83	91
100	100	53.14	58.05
	200	57.87	58.47
	300	65.70	69.06
200	100	56.43	25.44
	200	57.22	31.11
	300	60.39	32.22

Table 2. Peak current abatement efficiency in CV experiments at BDD electrode carried out in electrolysed solutions resulted in the electrochemical degradation of DCF at Ti/RuO$_2$/SnO$_2$-Sb$_2$O$_5$-RuO$_2$ anodes at various current densities and 120 min of electrolysis

DCF concentration of initial solution / mg/L	Current density / A/m^2	Peak current abatement efficiency at E = + 0.7 V/SCE / %	Peak current abatement efficiency at E = + 1 V/SCE / %
10	100	84.99	72.70
	200	95.56	84.91
	300	-	-
50	100	92.10	74.43
	200	93.00	80.65
	300	96.89	90.13
100	100	84.40	81.10
	200	84.40	86.25
	300	91.57	87.58
200	100	53.36	44.88
	200	92.69	82.00
	300	93.54	84.88

The peak current abatement efficiency at + 0.7 V/SCE and + 1 V/SCE at various DCF concentrations of initial solutions and various current densities for the DSA electrodes are listed in Tables 1 and 2. For both anodic compositions the abatement of peak current took place faster at + 0.7 V/SCE than at + 1 V/SCE overwhelming, possibly as a result of by-products yielding.

Concerning the effectiveness of the DSA electrodes in mineralization/degradation of DCF expressed as peak current abatement efficiency, Ti/RuO_2-TiO_2 anodes were the best at 10 mg/l DCF in the initial solution, comparable with $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ at 50 mg/L and less effective than $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ at 100 and 200 mg/L. This behaviour is probably due to the different ways in which the organics oxidation occurs. At Ti/RuO_2-TiO_2 anodes the organics oxidation is carried out via higher oxide generation, while at $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ are generated hydroxyl radicals.

CONCLUSIONS

The CV proved that is a rapid tool for assessing electrochemical degradation of DCF at DSA electrodes. The CVs of BDD in solutions resulted from electrochemical degradation of DCF at Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ anodes were recorded.
The analysis of CVs and the peak current abatement efficiency revealed a mineralization process along the degradation of DCF during the electrochemical oxidation of DCF at Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ anodes. Also, the by-products yielding were suggested.
Based on the peak current abatement efficiency calculated at $+ 0.7$ V/SCE and $+ 1$ V/SCE the most effective for degradation of DCF of 100 and 200 mg/L was $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ anode for any current density of 100, 200 and 300 A/m^2 and 120 mintes of electrolysis.

ACKNOWLEDGEMENTS

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