

## ELECTROCHEMICAL METHODS APPLIED TO PHARMACEUTICALLY ACTIVE COMPOUNDS DEGRADATION FROM WASTEWATERS

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### Abstract

The release of the pharmaceuticals in the environment is a topic of growing concern. The representative sources of pharmaceuticals in the environment are: human medicine (untreated sewage, wastewater and hospital effluent), veterinary medicine (wastewater, untreated sewage) and effluents of pharmaceutical production facilities. Some of pharmaceutically active compounds have negative impact on living organisms and ecosystems. Thus, it is important to pretreat the wastewater with content of pharmaceuticals prior to its discharge to the sewer system. The electrochemical methods are ones of the promising methods of removing pharmaceuticals from the wastewater. This paper was focused on the electrochemical degradation of the diclofenac (DCF) by using dimensionally stable anodes (DSA). DCF is a non-steroidal anti-inflammatory drug used in extent scale worldwide and it was found as persistent waste in the aquatic environment. The composition of DSA was  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  and the electrodes were prepared by thermal decomposition of appropriate precursors. The experiments were carried out in basic medium by using solutions of 50 and 100 mg/L DCF in 0.1 M  $\text{Na}_2\text{SO}_4$  as supporting electrolyte. The applied current densities were 100, 200 and 300  $\text{A/m}^2$  at various electrolysis times. The degradation process of DCF was assessed by recording the UV spectra and determining the total organic carbon (TOC). At 300  $\text{A/m}^2$  and 120 min of electrolysis for each initial concentration the DCF mineralization was about 40 - 50%.

**Keywords:** electrochemical methods, dimensionally stable anodes, diclofenac

### 1. Introduction

The presence of the pharmaceutically active compounds (PhACs) in the environment has given a special attention in the past years. Thus, intensive research on pharmaceuticals started because they are biologically active and persistent substances which have been recognized as a continuing threat to environmental stability [1,2].

PhACs are detected in surface waters and the sewage effluents at very low concentrations, from below 1 ng/L up to a few  $\mu\text{g/L}$  [2-5], and this is the reason because PhACs are called “micro-pollutants”.

Because of their properties PhACs exhibits bioaccumulation and toxic effects in aquatic and terrestrial ecosystems. PhACs have been shown to be present in the environment at levels that are associated with deleterious effects in aquatic organisms [6].

Among the non-steroidal anti-inflammatory drugs, diclofenac (DCF) shows the most acute toxic nature with effects being observed at concentrations below 100 mg/L. Chronic toxicity trials performed on rainbow trout evidenced cytological changes in the liver, kidneys and gills after 28 days of exposure to just 1 µg/L of diclofenac. For a concentration of 5 µg/L renal lesions were evident as well as drug bioaccumulation in the liver, kidneys, gills and muscle [1].

The presence of PhACs in the environment is undesired. Consequently, it is necessary to pretreat the wastewaters prior the discharge to the sewage treatment plant because this is ineffective for PhACs removal. The electrochemical methods are promising for the removal of organics from wastewaters. The advantages of anodic oxidation make it attractive. Thus, anodic oxidation does not require adding a large amount of chemicals to wastewater, it has not tendency of producing secondary pollution and fewer accessories required [7].

The effectiveness of the anodic oxidation is strongly dependent on the choice of electrode material. Dimensionally stable anodes (DSA) are promising materials for many anodic oxidation of organics and have been classified as “active” or “non-active” [8].

The aim of this paper was the removal of DCF in basic medium by anodic oxidation at Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> DSA electrodes.

## **2. Experimental**

### *2.1. Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> electrodes preparation*

The electrodes were prepared using titanium plates as a support. The plates were treated by sand-blasting followed by a chemical treatment with technical hydrochloric acid 15% for 20 minutes under boiling. Then they were washed with water, distilled water, absolute ethylic alcohol reagent grade (Chimopar Bucuresti). They were dried in open air and the precursors solution was brushed onto their surface. The precursors solution was obtained by dissolving RuCl<sub>3</sub>.nH<sub>2</sub>O (Fluka) and TiCl<sub>4</sub> (Carlo Erba) in the solution containing hydrochloric acid (37%) and isopropanol reagent grade (Chimopar Bucuresti). The molar ratio Ru:Ti in precursors solution was 30:70. The anodic material was further treated by heating at 110 °C in a drying cabinet. After that, the electrode was treated at 450-480 °C for 10 minutes to decompose the salt from precursors solution. This cycle brushing – drying – thermal decomposition was repeated 15 times. Finally, a thermal treatment was applied for 1 hour to stabilize the oxide film.

### *2.2. Electrolyses*

DCF (2-[2',6'-dichlorophenyl]amino]phenylacetic acid) was supplied by Amoli Organics Ltd as sodium salt. The sodium sulphate and sodium hydroxide were supplied by Riedel de Haen and they were reagent grade. The solutions were prepared with distilled water.

The electrolyses were carried out in a Plexiglas cell by using two DSA anodes and three stainless steel cathodes at 1 cm gap. Active surface area was 38 cm<sup>2</sup>. Experiments were carried out by applying current densities of 100, 200

and 300 A/m<sup>2</sup> at electrolysis times of 30, 60, 120 minutes, respectively. Electrolyses were carried out in solutions of 50 and 100 mg/L DCF in 0.1 M Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte. The pH of these working solutions was 11.

### 2.3. Analytical methods

Total organic carbon (TOC) was monitored by a TOC analyzer (Shimadzu - TOC-VCPH) computer controlled.

The UV spectra were recorded by A Specord 205 - Analytic Jena spectrophotometer computer controlled.

## 3. Results and discussions

Chemical structure of DCF is shown in Fig.1.

The shape of the absorption spectra in UV range of DCF solutions resulted during the degradation of the pollutant at Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> anodes are shown in Figs.2 and 3.

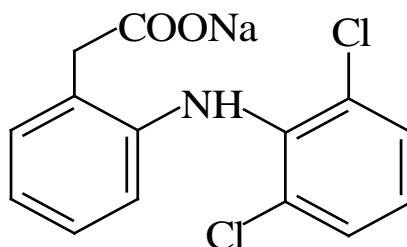


Fig.1. Chemical structure of DCF

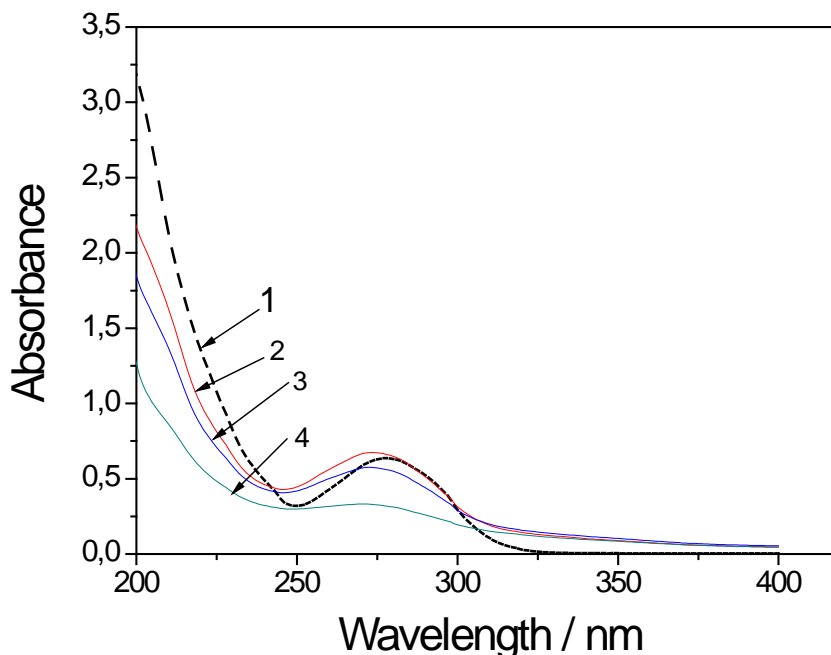
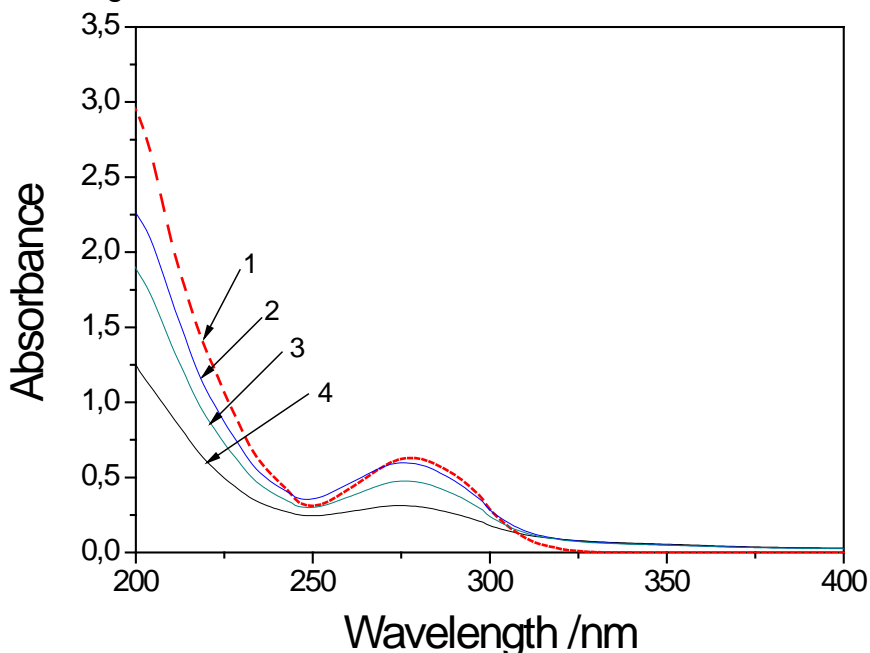


Fig.2. Spectra in UV range of solutions of DCF in 0.1 M Na<sub>2</sub>SO<sub>4</sub> (dilution 1:2.5) working sol.: 50 mg/L DCF in 0.1 M Na<sub>2</sub>SO<sub>4</sub>; pH of working sol.: 11; current density: 200 A/m<sup>2</sup>; electrolysis time : 1 - initial solution, 2 – 30 minutes, 3 - 60 minutes, 4 - 120 minutes

The spectrum of DCF in 0.1 M Na<sub>2</sub>SO<sub>4</sub> recorded in UV range displayed a maximum of absorbance at 278 nm. Figs. 2 and 3 reveal that during the degradation of DCF at Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> anodes the maximum of absorbance had higher values than the working solution or almost the same at 30 minutes of electrolysis because of intermediates formation. As the electrolysis time increased the maximum of absorbance decreased that prove the further intermediates degradation.



**Fig.3.** Spectra in UV range of solutions of DCF in 0.1 M Na<sub>2</sub>SO<sub>4</sub>(dilution 1:5) working sol.: 100 mg/L DCF in 0.1 M Na<sub>2</sub>SO<sub>4</sub>; pH of working sol.: 11; current density: 300 A/m<sup>2</sup>; electrolysis time : 1 - initial solution, 2 – 30 minutes, 3 - 60 minutes, 4 - 300 minutes

The above findings match the values of the absorbances listed in Tables 1 and 2. Also, it can be noticed that for each current density as the electrolysis time increased the A<sub>278</sub> decreased both for 50 mg/L and 100 mg/L DCF. The lowest values for A<sub>278</sub> were recorded at 120 minutes of electrolysis for each current density.

**Table 1.** Values of absorbance at 278 nm of DCF solutions (dil. 1:2.5) working solution: 50 mg/L DCF in 0.1 M Na<sub>2</sub>SO<sub>4</sub>; pH of working solution: 11

DCF* concentration/ mg/L	A <sub>278</sub> *	Current density / A/m <sup>2</sup>	Time / min	A <sub>278</sub>
50	0.63	100	30	0.66
			60	0.63
			120	0.56
		200	30	0.66
			60	0.56
			120	0.31
		300	30	0.58
			60	0.44
			120	0.16

\*values for working solution

**Table 2.** Values of absorbance at 278 nm of DCF solutions (dil. 1:5)  
 working solution: 100 mg/L DCF in 0.1 M Na<sub>2</sub>SO<sub>4</sub>; pH of working solution: 11

DCF* concentration/ mg/L	A <sub>278</sub> *	Current density / A/m <sup>2</sup>	Time / min	A <sub>278</sub> **
100	0.63**	100	30	0.60
			60	0.51
			120	0.45
		200	30	0.60
			60	0.52
			120	0.40
		300	30	0.59
			60	0.47
			120	0.30

\*values for working solution

The evolution of absorption spectra in UV range suggested the mineralization of DCF during the electrochemical degradation of DCF and thus the TOC of electrolysed solutions was monitored. The results are listed in Table 3. For each concentration, the removal of TOC efficiency increased as the current density increased and the best results were obtained at 120 minutes of electrolysis in accordance with the expectations.

**Table 3.** Working conditions, TOC variation and TOC removal efficiency during the anodic oxidation of DCF on Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> electrodes at 120 min electrolysis time

DCF* concentration/ mg/L	TOC*/ mgC/L	Current density / A/m <sup>2</sup>	Cell voltage / V	TOC / mgC/L	TOC removal efficiency/ %
50	27.04	100	3.2	20.98	22.41
		200	3.7	19.45	28.06
		300	4.1	15.45	42.86
100	55.07	100	3.2	43.23	21.49
		200	3.7	33.93	38.38
		300	4.1	28.53	48.19

\*values for working solution

### Conclusions

The paper dealt with the degradation of DCF by electrochemical methods. The anodic oxidation was carried out by using Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> DSA electrodes prepared by thermal decomposition of appropriate precursors and working solutions of 50 and 100 mg/L DCF in 0.1 M Na<sub>2</sub>SO<sub>4</sub>. The working solution pH was 11. The current densities were 100, 200 and 300 A/m<sup>2</sup>, and the electrolysis time was 30, 60 and 120 minutes.

The experiments proved the mineralization of the pollutant and the best results for TOC removal efficiency were obtained at 300 A/m<sup>2</sup> and 120 minutes of electrolysis: 42.86 mg C/L for the working solution of 50 mg/L DCF and 48.19 mg C/L for the 100 mg/L DCF one.

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## TREATMENT OF POLLUTANT EMISSIONS IN A BIOTRICKLING FILTER WITH A MOVING BED – PILOT VERIFICATION

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### Abstract

This study was aimed at testing a possibility of using a biotrickling filter with a moving bed for simultaneous treatment of waste air and waste water. For those purposes a laboratory biotrickling filter with a moving bed was constructed. After inoculating of the laboratory biotrickling filter long-term organic load tests were performed aimed at finding the maximum organic load of biotrickling filter which the biotrickling filter is operated with with high efficiency. The aim of the second test was testing the possibility of simultaneous removal of some odour compounds from waste air and waste water treatment. On the basis of operating parameters of the laboratory biotrickling filter and results of the long-term organic load tests two pilot biotrickling filters with a moving bed were designed and constructed. Subsequently they were installed in operating conditions in production of driving wheels and in a farm.