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REMOVAL OF PHARMACEUTICALS FROM WASTEWATERS BY ELECTROOXIDATION

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ABSTRACT

The removal of the non-steroidal anti-inflammatory drug diclofenac (DCF) was carried out by electrooxidation on Dimensionally Stable Anodes (DSA) with the composition $Ti/Ru_{0.3}Ti_{0.7}O_2$. The DSA electrodes were obtained by thermal decomposition of the appropriate precursors. The electrolyses were carried by using solutions of 100 mg/L DCF in 0.1 M Na_2SO_4 supporting electrolyte in acidic medium at various current densities and electrolysis times. The removal of DCF was assessed by recording UV-VIS spectra and chemical oxygen demand (COD) determination of the electrolysed solutions. The results showed the mineralization of the DCF during the electrooxidation on $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrodes.

INTRODUCTION

In the recent years pharmaceuticals have became a novel class of water pollutants because of their potential effects on the environment and human health at very low level of concentration [1-5].

Diclofenac (DCF) belongs to non-steroidal anti-inflammatory drugs and it is worldwide used. This group of pharmaceuticals are often found as persistent toxic waste [6]. It is known that DCF has effect on the environment. Thus, the catastrophic decline of Gyps vultures in Northern India is connected to DCF [7,8].

The pharmaceutical manufacturing industry produces a wide range of products to be used as human as and animal medications. The wastewaters from the pharmaceutical manufacturing industry may contain high organic load [9]. Therefore, it is necessary to develop effective technologies before to discharge such effluents into the sewage system [7].

A promising technology that can lead to the abatement of pharmaceuticals in the wastewaters is the electrochemical one. Electrochemical processes have major advantages for the wastewater treatment: versatility, energy efficiency, suitable to automation, environmental compatibility and cost effectiveness.

The effectiveness of the electrochemical processes for the organics degradation depends on the choice of electrodes material. Dimensionally Stable Anodes (DSA) have attracted attention as electrodes for organics degradation because they exhibits great stability under electrolysis conditions [10] and they are exceptional from the point of view of the versatility [11].

The aim of this paper was the removal of DCF in acidic medium by electrooxidation at $Ti/Ru_{0.3}Ti_{0.7}O_2$ DSA electrodes.

MATERIALS and METHODS

The DSA electrodes used in these experiments were $Ti/Ru_{0.3}Ti_{0.7}O_2$. The electrodes were prepared by thermal decomposition of appropriate precursors. The preparation of the electrodes was reported in our previous work [12].

DCF (2-[2',6'-dichlorophenyl)amino]phenylacetic acid) was supplied by Amoli Organics Ltd as sodium salt and sodium sulphate by Merck. Distilled water was used for the preparation of the solutions.

The electrolyses were accomplished by using two DSA anodes and three stainless steel cathodes at 1 cm gap. Active surface area was 38 cm^2. Experiments were carried out by applying current densities of 100, 200 and 300 A/m^2 at electrolysis times of 30, 60, 120 minutes, respectively. Electrolyses were carried out in solutions of 100 mg/L DCF in 0.1 M Na_2SO_4 as supporting electrolyte.

The pH of the working solutions was 5.5. The solutions were prepared with distilled water and Na_2SO_4 (Reactivul Bucureşti) reagent grade. A Specord 205 - Analytic Jena spectrophotometer controlled by computer recorded the UV spectra.

RESULTS

The chemical structure of DCF is shown in Fig.1 and the spectrum of DCF in 0.1 M Na_2SO_4 recorded in UV range in Fig.2.

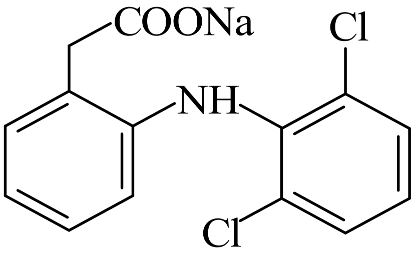

Fig.1. Chemical structure of DCF

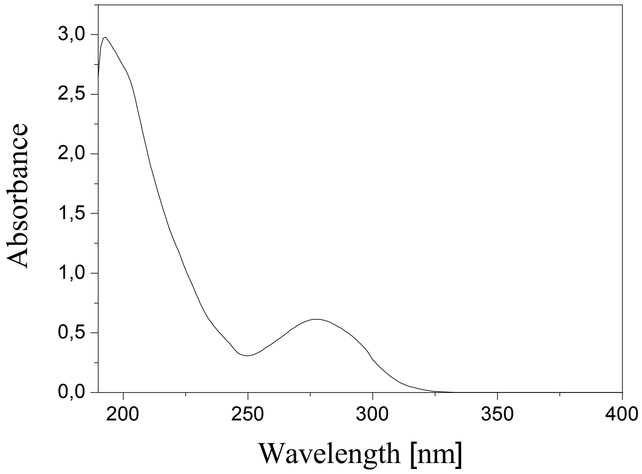

Fig.2. UV spectrum of DCF in 0.1 M Na_2SO_4
DCF concentration - 100 mg/L, dilution - 1:5

The UV spectrum of the DCF in 0.1 M Na_2SO_4 displayed two absorbance peaks at 277 nm and 193 nm. The degradation process of DCF is dependent on electrolysis time and current density. Thus, the variation of these parameters influenced the UV spectra shape during the electrooxidation on $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrodes. The UV spectra of the electrolysed solutions are shown in Fig.3-5.

It can be observed the decrease of the absorbance with the increase of the current density and electrolysis time. Though, it is necessary to mention that the degradation of DCF occurred at a very small extent after 30 minutes of electrooxidation or almost at the same extent both at 30 and 60 minutes of electrooxidation.

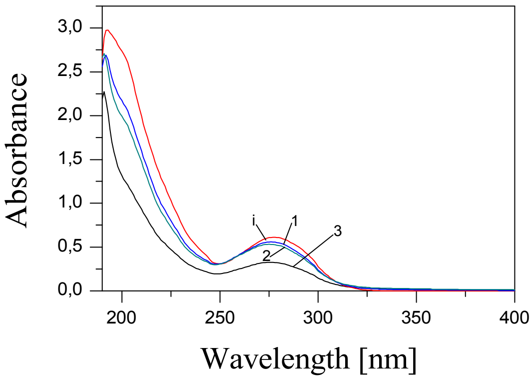

Fig. 3. UV spectra of DCF in 0.1 M Na_2SO_4
anode: $Ti/Ru_{0.3}Ti_{0.7}O_2$; initial concentration: 100 mg/L;
initial pH: 5.5; dilution - 1: 5;
current density: 100 A/m^2; electrolysis time:
i – 0 min; 1 - 30 min; 2 - 60 min; 3 – 120 min

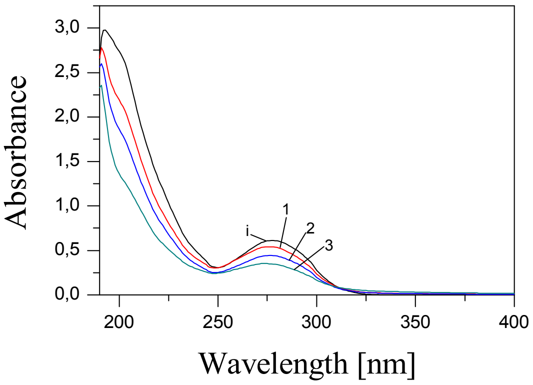

Fig. 4. UV spectra of DCF in 0.1 M Na_2SO_4
anode: $Ti/Ru_{0.3}Ti_{0.7}O_2$; initial concentration: 100 mg/L;
initial pH: 5.5; dilution - 1: 5;
current density: 200 A/m^2; electrolysis time:
i – 0 min; 1 - 30 min; 2 - 60 min; 3 – 120 min

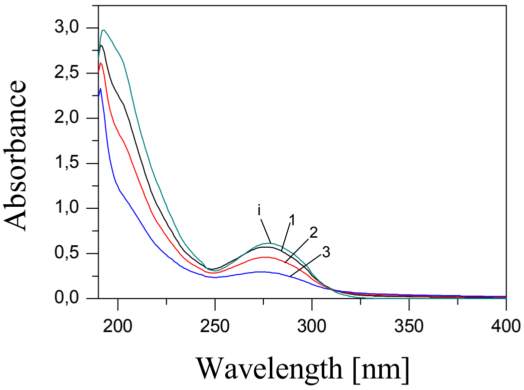

Fig. 5. UV spectra of DCF in 0.1 M Na_2SO_4
anode: $Ti/Ru_{0.3}Ti_{0.7}O_2$; initial concentration: 100 mg/L; initial pH: 5.5; dilution - 1: 5;
current density: 300 A/m^2; electrolysis time: i – 0 min; 1 - 30 min; 2 - 60 min; 3 – 120 min

Table 1. Working conditions and COD variation during the electrooxidation of DCF on $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrodes
initial concentration - 100 mg/L DCF, initial COD – 140 mg O_2/L

Current density / A/m^2	Electrolysis time / min	Cell voltage / V	COD / mgO_2/L
100	30	3.2	113.28
	60	3.2	102.38
	120	3.2	59.31
200	30	3.7	107.73
	60	3.7	80.79
	120	3.7	59.31
300	30	4.0	113.28
	60	4.0	91.58
	120	4.0	59.31

Also, the degradation process of the DCF was assessed by COD of the electrolysed solutions. The results are shown in Table 1. The COD decreased with the increase of the electrolysis time for each current density. Also, no important differences of COD can be noticed among the current densities for the electrolysis time of 30 and 120 minutes. The situation is not the same for 60 minutes of electrolysis probably because of different formation rates of intermediates.

CONCLUSIONS

The paper dealt with the removal of non-steroidal anti-inflammatory drug DCF by electrooxidation on $Ti/Ru_{0.3}Ti_{0.7}O_2$ DSA electrodes in acidic medium. The applied current densities were 100, 200 and 300 A/m^2 at 30, 60 and 120 minutes of electrolysis.

The UV spectra and the COD values of the electrolysed solutions revealed the mineralization of DCF during the electrooxidation process and the best result for COD abatement was 61.45% at 300 A/m^2 and 120 minutes of electrolysis.

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