Diclofenac Removal at Low Concentrations from Wastewaters by Electrochemical Oxidation

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The aim of this paper was to apply the electrochemical oxidation on Dimensionally Stable Anodes (DSA), Ti/RuO_2-TiO_2 and Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2, to remove pharmaceuticals at low concentrations from wastewaters. Diclofenac (DCF), which is recalcitrant to biological degradation, was chosen as a pharmaceuticals model. The process was followed by recording the ultraviolet (UV) spectra and assessing the DCF concentration in the electrolyzed solutions by high-performance liquid chromatography (HPLC) with ultraviolet-visible (UV-VIS) detection. The best results were obtained in the case of Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 anodes.

Keywords: electrochemical oxidation, Dimensionally Stable Anodes, diclofenac

Pharmaceuticals are used on a wide scale and their use and diversity is raising yearly. They are designed to have a specific pathway of action and also certain persistence in humans and animals. Because of these features a great part of pharmaceuticals pass unchanged through their bodies and thus, by urine and excrements, they reach wastewaters [1,2].

Concerns related to the presence of pharmaceuticals in water are due to their toxic effects upon the aquatic organisms detected at low levels of concentration [3-5]. Most of pharmaceuticals pass unchanged through wastewater treatment plants and thus they emerge into waters bodies [6,7].

Because of the increased performances of the analytical chemistry the investigation regarding the pharmaceuticals determination in commercial products [8-10] and pharmaceuticals presence in the environment are nowadays possible [11,12]. The pharmaceuticals were found in the range of ng/L-μg/L in the effluents of wastewater treatment plants and surface waters [13].

The electrochemical methods are efficient tools for wastewater treatment as it was reported [14,15]. The main advantages of the electrochemical methods are versatility, amenability to automation, applicability to various pollutants, easy handling and no high pressures and temperatures are needed. Also, the electrochemical methods are environmentally compatible, the main reagent used is the electron which is a clean reagent [16,17].

The aim of this paper was to apply the anodic oxidation to removal of the diclofenac (DCF), a pharmaceutically active compound, at low level of concentrations from wastewaters by using Dimensionally Stable Anodes (DSA).

Experimental part

DSA anodes preparation

The DSA anodes having the compositions Ti/RuO_2-TiO_2 (molar ratio in the precursors solution 30:70) and Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 (molar ratio in the precursors solution 94:3:3) were prepared by thermal decomposition of appropriate precursors. The DSA anodes preparation was related extensively in our previous works [18,19] with the notice that for Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 in the mixture of the precursors was also introduced the precursor $RuCl_3 \cdot nH_2O$ (Fluka).

Electrolyses

Diclofenac (DCF) (2-[2',6'-dichlorophenyl) amino] phenylacetic acid) was supplied by Amoli Organics Ltd as sodium salt. The Na_2SO_4 and NaOH 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^2 and the power supply was DC HY 3003. Experiments were carried out by applying current densities of 100, 200 and 300 A/m^2 at electrolysis times of 30, 60, 120 min, respectively. The electrolysis set-up is schematically shown in figure 1.

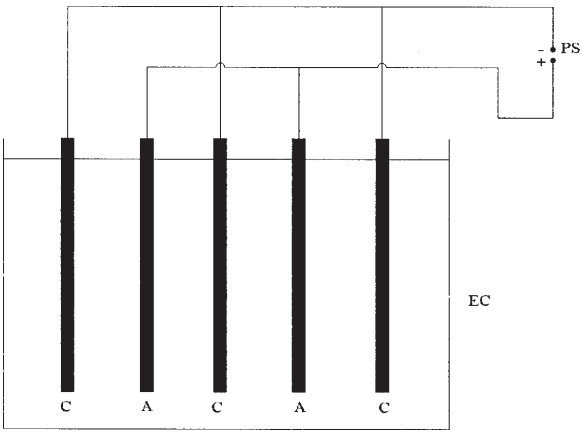

Fig.1. Batch experimental set-up PS – DC power supply, C - cathode, A-anode, EC-electrolysis cell

Electrolyses were carried out in simulated solutions and spiked effluent of a wastewater treatment plant (DCF-EWWTP) of 75 mL. The simulated solutions were of 1 mg/L DCF in 0.1 M Na_2SO_4 as supporting electrolyte, and *p*H of 5.8 and 11, respectively. The DCF-EWWTP used in the experiments had the characteristics: 1 mg/L DCF, 14.2 mg/L Na_2SO_4 and *p*H of 11.

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Analytical methods

The UV spectra were recorded by A Specord 205 - Analytik Jena spectrophotometer computer controlled for monitoring the process.

The assessment of the DCF in the electrolysed solutions was carried out by high-performance liquid chromatography (HPLC) with ultraviolet-visible (UV-VIS) detection. It was used a HPLC Agilent 1100 system. The detection was performed with an UV-VIS detector (MWD) with variable wavelength and aptitude for recording simultaneously at five different wavelengths.

The instrument control, acquisition, processing and report of data were performed by using ChemStation software. A LiChrosphere® 100 RP-18 C18 column (125 mm x 4 mm, 5μm), purchased from Merck (Darmstadt, Germany), was used for chromatographic separation. Column temperature was 25 ć %C and the injection volume 20 μL. The mobile phase consisted of acetonitrile (solvent B) and 50 mM potassium dihydrogen phosphate in water (solvent A). Flow rate was 1 mL/min. The gradient elution programme is presented in table 1.

Table 1
GRADIENT ELUTION PROGRAMME

Time (min)	Solvent A (%)	Solvent B (%)
0	85	15
4	85	15
9	75	25
19	55	55
35	60	40

Results and discussions

Chemical structure of DCF is shown in figure 2. As it is shown in figures 3 and 4 the UV spectrum of DCF is typical for benzene derivates and it displays two maxima of absorbance at 193 and 277 nm [20, 21].

The shape of UV spectra of the simulated solutions that underwent electrochemical treatment on Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 in acidic and basic medium is presented in figures 5-8.

Regarding the Ti/RuO_2-TiO_2 anodes it can be observed the decrease of the maximum of absorbance as the electrolysis time increased. It was noticed only one exception at 100 A/m² in acidic medium when the maximum of absorbance after 60 min of electrolysis had a higher value than after 30 min . This can be assigned to the formation of some oxidation products that have an extinction coefficient higher than those of DCF.

Also, in acidic medium one could observe a shift of the maximum of absorbance from 277 nm to 274, 271, 266, and 261 nm, respectively for any of applied current densities, and in basic medium from 277 nm to 274 nm (table 2). This shift of the maximum could be attributed to the formation of compounds resulted from the partially cleavage of benzene rings and partially degradation of these compounds [22,23].

In acidic medium at current densities of 200 and 300 A/m² and 120 min of electrolysis the maxima disappeared from the spectrum that proved further degradation of oxidation products. In basic medium the DCF degradation process occurred more effective, the maxima disappeared from the spectrum even at 60 min of electrolysis and 300 A/m².

Similar to Ti/RuO_2-TiO_2 anodes, in case of $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 anodes the shift of the maximum of absorbance to smaller wavelength values: in acidic medium from 277 nm to 273, 272 and 271 nm, and in basic medium from 277 nm to 272 nm (table 3), occurred as a result of formation of electrochemical degradation products, as it was mentioned before.

In acidic medium, the spectrum had absorbance maxima that exceeded in intensity the maximum of the initial absorbance at 100 and 200 de A/m², and in basic medium only at 100 de A/m². The explanation could be that at these current densities formation of oxidation products that had extinction coefficient higher than those of DCF solution occurred. As the electrolysis time and current density increased these compounds were still degraded until the maxima disappeared from spectra after 120 min of electrolysis and current densities of 200 and 300 A/m² in acidic medium, and in basic medium at 200 and 300 A/m² and duration of electrolysis of 60 and 120 min, respectively. The process occurred with the highest rate at 300 A/m², as it can be seen in table 3.

The comparative analysis of absorbance maxima, recorded for initial pH of reaction medium either acidic or basic, led to the finding that the degradation process occurred more effectively in basic medium, the maximum of absorbance disappeared from the spectrum after a shorter time of electrolysis in basic medium.

Regardless the initial *p*H and the anodic composition, the absorption curves had a descendant progress in benzoidic region that showed the electrochemical process evolution with advanced oxidation of aromatic rings.

The removal of DCF in simulated solutions and DCF-EWWTP was quantified by determining the concentration

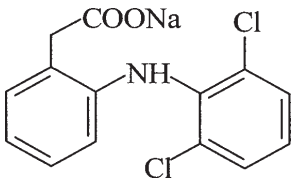

Fig.2. Chemical structure of DCF

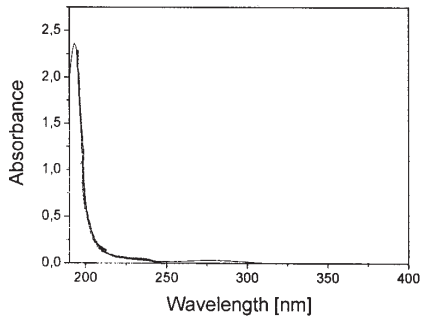

Fig.3. UV spectrum of DCF in 0.1 M Na_2SO_4; DCF concentration: 1 mg/L DCF; UV range: 190-400 nm

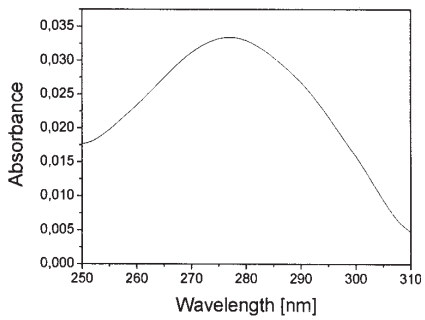

Fig.4. UV spectrum of DCF in 0.1 M Na_2SO_4; DCF concentration: 1 mg/L DCF; UV range: 250-310 nm

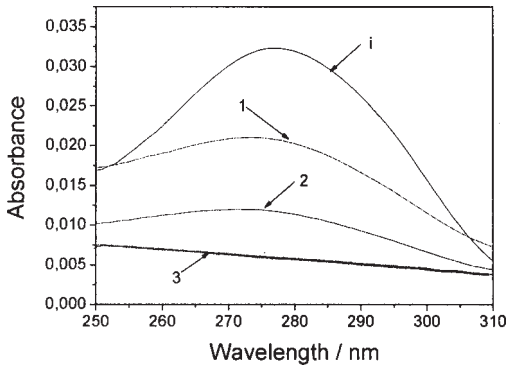

Fig.5. UV spectra of simulated solutions of DCF in 0.1 M Na_2SO_4 anode: Ti/RuO_2-TiO_2; working solutions: 1 mg/L DCF in 0.1 M Na_2SO_4; *p*H of working solutions: 5.8; current density: 200 A/m^2; electrolysis time: i – 0 min, 1 – 30 min, 2 - 60 min, 3 - 120 min

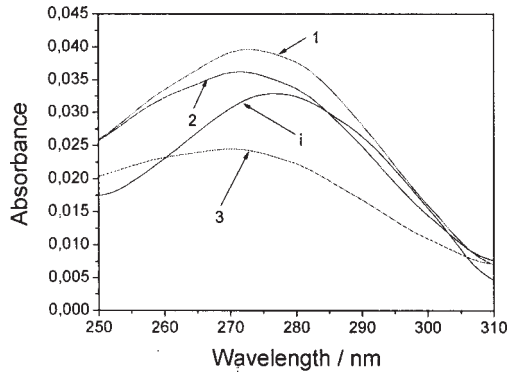

Fig.7. UV spectra of simulated solutions of DCF in 0.1 M Na_2SO_4 anode: Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2; working solutions: 1 mg/L DCF in 0.1 M Na_2SO_4; *p*H of working solutions: 5.8; current density: 100 A/m^2; electrolysis time: i – 0 min, 1 – 30 min, 2 - 60 min, 3 - 120 min

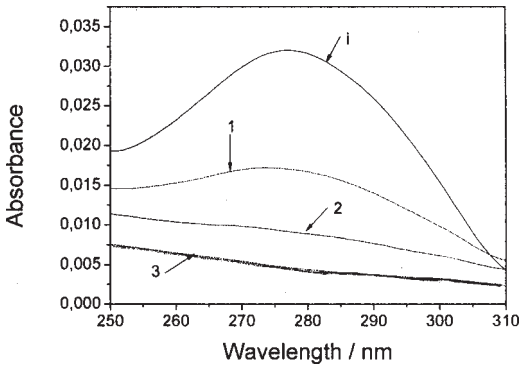

Fig.6. UV spectra of simulated solutions of DCF in 0.1 M Na_2SO_4 anode: Ti/RuO_2-TiO_2; working solutions: 1 mg/L DCF in 0.1 M Na_2SO_4; *p*H of working solutions: 11; current density: 300 A/m^2; electrolysis time: i - 0 min, 1 - 30min, 2 - 60 min, 3 - 120 min

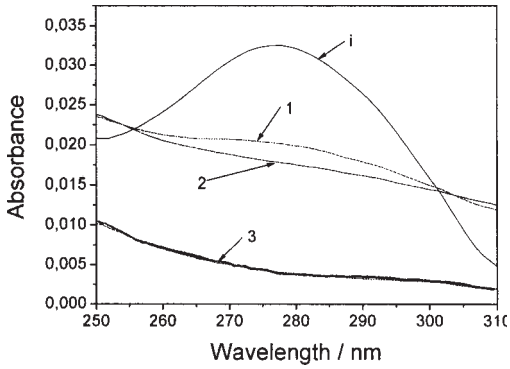

Fig.8. UV spectra of simulated solutions of DCF in 0.1 M Na_2SO_4 anode: Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2; working solutions: 1 mg/L DCF in 0.1 M Na_2SO_4; *p*H of working solutions: 11; current density:300 A/m^2; electrolysis time: i – 0 min, 1 – 30 min, 2 - 60 min, 3 - 120 min

Table 2

WORKING CONDITIONS, WAVELENGTH AND ABSORBANCE FOR DCF DEGRADATION ON Ti/RuO_2-TiO_2 ANODES

Anodic composition/pH	Current density (A/m^2)	Electrolysis time (min)	Wavelength (nm) / Absorbance				
			261	266	271	274	277
-	-	0	-	-	-	-	0.032
Ti/RuO_2-TiO_2/acidic	100	30	-	-	-	0.021	-
		60	-	0.026	-	-	-
		120	0.013	-	-	-	-
	200	30	-	-	-	0.021	-
		60	-	-	0.012	-	-
		120	-	-	-	-	-
	300	30	-	0.024	-	-	-
		60	-	0.012	-	-	-
		120	-	-	-	-	-
Ti/RuO_2-TiO_2/basic	100	30	-	-	-	0.027	-
		60	-	-	-	0.019	-
		120	-	-	-	0.010	-
	200	30	-	-	-	0.021	-
		60	-	-		0.011	-
		120	-	-	-	-	-
	300	30	-	-	-	0.017	-
		60	-	-	-	-	-
		120	-	-	-	-	-

of DCF in electrolysed solutions by HPLC with UV-VIS detection method. As it is shown in table 4, regardless the anodic composition, the removal efficiency of DCF is higher in basic medium. Between the two anodic compositions, the most effective in degradation/removal of DCF from simulated solutions was Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2.

The removal efficiency of DCF from DCF-EWWTP at current density of 300 A/m^2 and 120 min of electrolysis on Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 anodes was lower than that reached in simulated solutions under the same conditions (table 4), which proved the influence of the matrix to which DCF belongs on removal process.

Anodic composition/pH	Current density (A/m^2)	Electrolysis time (min)	Wavelength (nm) / Absorbance			
			271	272	273	277
-	-	0	-	-	-	0.032
$Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2/ acidic	100	30	-	-	0.039	-
		60	0.036	-	-	-
		120	0.024	-	-	-
	200	30	-	0.034	-	-
		60	-	0.026	-	-
		120	-	-	-	-
	300	30	0.029	-	-	-
		60	0.018	-	-	-
		120	-	-	-	-
$Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2/ basic	100	30	-	0.043	-	-
		60	-	0.032	-	-
		120	-	0.020	-	-
	200	30	-	0.030	-	-
		60	-	-	-	-
		120	-	-	-	-
	300	30	-	0.020	-	-
		60	-	-	-	-
		120	-	-	-	-

Table 3
WORKING CONDITIONS, WAVELENGTH AND ABSORBANCE FOR DCF DEGRADATION ON $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 ANODES

Working solution	Anodic composition	pH of working solution	DCF concentration in the electrolysed working solution (mg/L)	DCF removal efficiency (%)
simulated solution	Ti/RuO_2-TiO_2	5.8	0.43	57
		11	0.29	71
simulated solution	$Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2	5.8	0.26	74
		11	0.14	86
DCF-EWWTP	$Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2	11	0.47	53

Table 4
DCF CONCENTRATION IN THE ELECTROLYSED WORKING SOLUTIONS CONCENTRATION WORKING SOLUTIONS: 1 mg/L DCF; CURRENT DENSITY: 300 A/m^2; ELECTROLYSIS TIME: 120 min

Conclusions

The results for DCF removal at low concentrations from simulated solutions and DCF-EWWTP by electrochemical oxidation on DSA showed good removal efficiency. Thus, the UV spectra analysis of electrolysed simulated solutions revealed the cleavage of bond between the benzene rings and advanced oxidation of aromatic rings.

Also, the UV spectra analysis of electrolysed simulated solutions showed that the degradation of DCF occurred with higher efficiency in basic medium regardless of the anodic composition and the most effective proved to be $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2. At a current density of 300 A/m^2, electrolysis time of 120 min and solution initial *p*H of 11, by using the anodic composition $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 the removal efficiency of DCF was 86 %.

The removal efficiency of DCF from the spiked effluent of a wastewater treatment plant by using the anodic composition $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 in the above mentioned conditions was 53 %.

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