Custom-made Dimensionally Stable Anodes for Diclofenac Electrochemical Degradation

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The aim of this paper was to assess the degradation of diclofenac (DCF), a non-biodegradable micro pollutant on dimensionally stable anodes (DSA), Ti/RuO_2-TiO_2 and Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2. The degradation process was assessed by examination of ultraviolet (UV) spectra and total organic carbon (TOC) analysis. Also, the assessment of DCF by-products in the electrolysed solutions was carried out by gas chromatography coupled to mass spectrometry (GC-MS). The aromatic ring opening and mineralization occurred.

Keywords: electrochemical degradation, dimensionally stable anodes, diclofenac

In January 2012 the European Commission proposed to add another fifteen priority substances to the list of pollutants that are monitored and controlled in surface waters in the European Union. Thus, certain pharmaceutical substances have been included in hazardous and priority substances management for the first time in history. The Directive 2013/39/EU stipulates that diclofenac, 17-beta-estradiol (E2) and 17-alpha-ethinylestradiol (EE2) to be included in the first watch list [1].

A source of non-biodegradable micro pollutants is the effluents from drug facilities. The pharmaceutical effluents are discharged in the sewerage systems and thus the non-biodegradable micro pollutants reach the waste water treatment plants. They pass unchanged through the wastewater treatment plants and thus they enter into the surface waters.

Diclofenac (DCF) is a non-steroidal anti-inflammatory drug that belongs to non-biodegradable micro pollutants. Unfortunately DCF has harmful effects upon the aquatic organisms as the studies regarding its ecotoxicology have proved.

Effects of the DCF on the marine mussel (*Mytilus spp.*) have been studied by Schmidt et al [2], who have found that DCF significantly induced lipid peroxidation indicating potential tissue damage. Also, the standard toxicity tests using the marine species *Vibrio fischeri, Skeletonema costatum* and *Tisbe battagliai* have shown differences in sensitivity to DCF in the mg/L range. Studies have demonstrated that DCF is the most cytotoxic for zebra mussel *(Dreissena polymorpha*), an aquatic invertebrate, among the four drugs used for *in vitro investigation:* atenolol, carbamazepine, diclofenac and gemfibrozil [3].

The low concentrations (ng/L) of non-steroidal anti-inflammatory drugs DCF and ibuprofen entering the river ecosystem over longer observation times, get tolerant communities of lower diversity and altered metabolic profile of microbial organisms [4]. The toxicity of most commonly detected pharmaceuticals in the aquatic environment, clofibric acid and DCF has been investigated in an Indian major carp *Cirrhinus mrigala* by exposing to drugs concentrations of μg/L [5]. The results suggest that both clofibric and DCF drugs induce significant changes on thyroid hormonal levels of *Cirrhinus mrigala.*

Islas-Flores et al. [6] have found out that DCF induces oxidative stress on the common carp (*Cyprinus carpio*), with the highest incidence of oxidative damage occurring in liver and gill. The effects of DCF have been studied in male fish *Hoplias malabaricus* after trophic exposure. The results suggest that DCF causes oxidative stress and reduced testosterone levels that can have a deleterious effect in aquatic organisms [7].

Because of harmful effects of DCF on aquatic organisms and the inefficiency of waste treatment plants to biodegrade DCF, it is necessary to remove or degrade this micro pollutant before pharmaceutical effluents reach the waste water treatment plants. As a consequence, there are many processes for removal or degradation of pharmaceuticals, especially DCF, in the literature: ultrafiltration/reverse osmosis followed by electrochemical oxidation of the reverse osmosis concentrate [8], irradiation technology [9,10], adsorption on hybrid materials [11,12] or on calcareous soils [13], advanced oxidation processes [14-17], combined processes based on hydrodynamic cavitation-heterogeneous photocatalysis or sequential biological degradation-solar photocatalytic oxidation processes [18,19].

The electrochemical methods are environment-friendly and could offer solution for remediation of effluents containing pharmaceuticals [20]. Also, the electrochemical methods have major advantages for the wastewater treatment: versatility, energy efficiency and suitable to automation. The performances of the electrochemical methods for the pharmaceuticals degradation depend on the electrode material. Dimensionally stable anodes (DSA) have attracted attention as electrodes for organics degradation because they have excellent mechanical, electrical and electrocatalytical properties.

This paper investigated the degradation of DCF by electrochemical oxidation at two compositions of DSA, Ti/RuO_2-TiO_2 and Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2, to get useful information for application of electrochemical methods to pharmaceutical effluents remediation.

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Experimental part

DSA preparation

The DSA 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 preparation was reported in our previous work [21].

Electrolyses

Diclofenac (DCF) (2-[2',6'-dichlorophenyl)amino] phenylacetic acid) was supplied by Amoli Organics Ltd as sodium salt. The Na_2SO_4 was 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 minutes, respectively.

Electrolyses were carried out in solutions of 50, 100 and 200 mg/L DCF, respectively, in 0.1 M Na_2SO_4 as supporting electrolyte. The pH of native solutions was 5.8.

Analytical methods

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

The total organic carbon (TOC) was monitored by a TOC analyzer (Shimadzu - TOC-VCPH).

The assessment of DCF by-products in the electrolysed solutions was carried out by gas chromatography coupled to mass spectrometry (GC-MS). The devices were a gas-chromatograph Agilent 7890A coupled to a mass ion trap Agilent 240MS. The preparation of organic extracts was carried out by liquid-liquid extraction with various solvents: hexane, mixture of hexane-dichloromethane and dichloromethane. The organic phases were re-collected and dried on anhydrous Na_2SO_4 to 10 mL. The Na_2SO_4 was washed with hexane, and then the solvent was re-collected with the sample. The electrolyzed solutions and analysed by GC-MS were obtained starting with an initial solution of 100 mg/L DCF in 0.1 M Na_2SO_4 that underwent electrolysis on DSA at 300 A/m^2 and up to 120 min duration.

Results and discussions

DCF Degradation

The chemical structure of DCF is shown in figure 1. The UV spectrum of DCF in 0.1 M Na_2SO_4 is shown in figure 2 and reveals two absorption bands with maxima at 193 nm and 277 nm. The absorption of maximum at 277 nm was used for the evaluation of the DCF degradation process with DSA versus initial concentration of DCF, current density and electrolysis time.

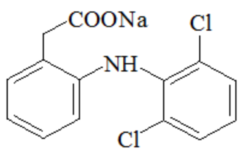

Fig. 1. Chemical structure of DCF

The formation of DCF degradation by-products and their further degradation is revealed by UV recorded spectra. Thus, the intensity of absorption at 277 nm for sample containing 50 mg/L DCF increased in the beginning of the process due to the formation of intermediary compounds with molar extinction coefficients greater than that of DCF, and then decreased against electrolysis time for both anodic compositions (figs. 3 and 4).

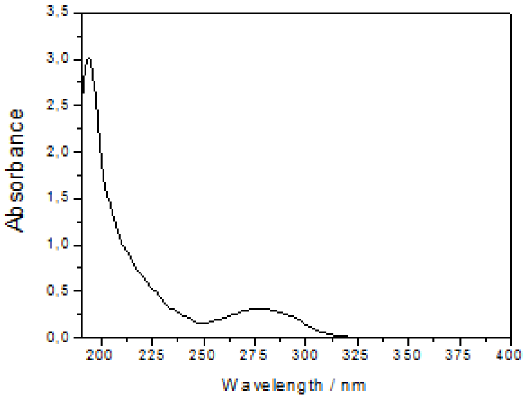

Fig. 2. UV spectrum of DCF in 0.1 M Na_2SO_4

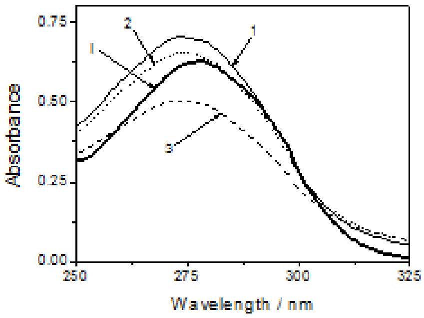

Fig.3. UV spectra of solution of 50 mg/L DCF in 0.1 M Na_2SO_4 anode: Ti/RuO_2-TiO_2; current density: 100 A/m^2; electrolysis time: i – 0 min, 1 – 30 min, 2 - 60 min, 3 - 120 min

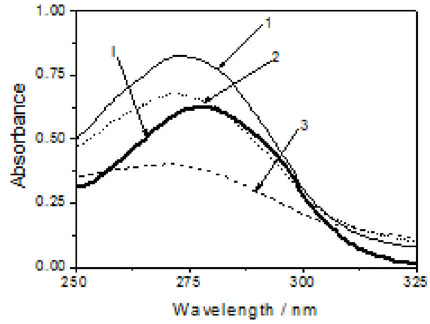

Fig.4. UV spectra of solution of 50 mg/L DCF in 0.1 M Na_2SO_4 anode: Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2; current density: 100 A/m^2; electrolysis time: i – 0 min, 1 – 30 min, 2 - 60 min, 3 - 120 min

The changes in spectra shape for samples with initial concentrations of 100 and 200 mg/L DCF are similar to those recorded for sample of 50 mg/L DCF. The yields of absorbance decreasing at 277 nm for the two anodic compositions are presented in table 1. As it was expected for both anodic compositions and all current densities, the progress of DCF degradation process developed as the electrolysis time increased.

The values of yields for absorptions decreasing show a more advanced process for sample of 200 mg/L DCF as compared to that containing 100 mg/L in the first 30-60 min for all current densities, but for higher electrolysis times the results are closer, table 1.

The global reaction rate of DCF electro degradation consists of simultaneous and successive reactions, with different kinetics. In UV spectra corresponding to the above samples the presence of some intermediary compounds is not observed: this shows that intermediary by-products formed in the first minutes are transformed with greater rates than those of their formation from DCF. The degradation of DCF's intermediates is very rapid in the first 30-60 min of electrolysis, the oxidation yield having an increasing evolution with the initial DCF concentration. For higher electrolysis time the efficiencies of absorptions decreasing at 277 nm are similar for the two concentrations, and this shows that the degradation process is slower between 60-120 min, in agreement with TOC, table 2.

By contrast, with Ti/RuO_2-TiO_2 for Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 anode and sample of 100 mg/L DCF after electrolysis during 30 min the formation of by-products with molar extinction coefficients greater than of DCF at 277 nm were observed for all current densities. Reaction rate is

Anodic composition	Current density (A/m^2)	Electrolysis time (min)	Concentration (mg/L DCF) / Absorption abatement efficiency / (%)	
			100	200
Ti/RuO_2-TiO_2	100	30	6.67	23.78
		60	13.72	34.55
		120	47.01	54.77
	200	30	11.73	32.8
		60	27.77	35.16
		120	43.07	45.98
	300	30	6.8	23.7
		60	25.62	31.22
		120	52.36	43.03
$Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$	100	30	*	0
		60	*	10.01
		120	22.62	23.2
	200	30	*	1.07
		60	10.69	18.99
		120	56.85	36.02
	300	30	*	9.12
		60	28.34	26.25
		120	77.22	59.96

*compounds with molar extinction coefficient greater than of DCF at 277 nm

Table 1
WORKING CONDITIONS AND ABSORPTION ABATEMENT EFFICIENCY AT 277 nm

Anodic composition	Current density (A/m^2)	Concentration (mg/L DCF) / TOC removal (%)		
		50	100	200
Ti/RuO_2-TiO_2	100	21.36	31.24	36.34
	200	40.04	42.52	43.8
	300	43.11	43.11	44.17
$Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$	100	7.19	16.9	31.46
	200	7.56	24.93	35.73
	300	12.99	36.57	39.73

Table 2
WORKING CONDITIONS AND TOC REMOVAL AT 120 MIN OF ELECTROLYSIS

dependent both of initial concentration and anodic composition. Higher absorptions observed for electrolysis with $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ anode shows the process is slower in this case and allows spectrophotometric recording of intermediary by-products with more intense absorptions than that of DCF. For longer electrolysis time like 60-120 min, advanced degradation of intermediary compounds takes place, and absorptions decreased significantly by comparison with the initial spectrum. Also, the absorption maximum at 277 nm is shifted to lower values at 273, 272, 271 and 270 due to the formation of intermediary by-products.

Similarly to the sample of 50 mg/L DCF, the shift of absorption maximum to lower wavelengths took place for the samples of other concentrations and all applied current densities. Thus, for 100 mg/L DCF at 300 A/m^2, electrolysis time of 120 min and anodic Ti/RuO_2-TiO_2 the absorption maximum shift at 273 nm and for $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ at 272 nm. 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 [21].

These observations are in agreement with the results of electrolyzed samples analysis by GC-MS. Electrolyzed samples were obtained from a solution with initial concentration 100 mg/L DCF in 0.1 M Na_2SO_4 after electrolysis with the two anodic compositions at current density of 300 A/m^2 for 120 min.

For both Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ the breaking of NH bond from the aromatic ring substituted with CH_2-COO^- group and carboxylic group mineralization took place. A few degradation by-products resulted from electrochemical oxidation on studied anodic compositions have the same structures, like 2, 6-dichloro-benzamine and 2, 6-dichlorophenyl-2H-Indol-2-one.

DCF Mineralization

The absorption variation at 277 nm is proportional with concentration and can be used for evaluation of DCF mineralization. The decrease of absorbance with maximum at 277 nm proved the degradation/mineralization of DCF. However, degradation by-products bring their contribution in spectra and the absorption decrease at 277 nm may not give true mineralization degree. For a correct evaluation of DCF mineralization the TOC analysis of electrolyzed samples was undertaken and the results are presented in table 2.

The best results for DCF mineralization on two anodic compositions were obtained at current density 300 A/m^2, electrolysis time of 120 min and 200 mg/L DCF. By theory, if one carbon atom from DCF molecule is mineralized TOC removed is 4.17% and for six carbon atoms the removal is 24.84% (DCF molecule contains 14 carbon atoms). By comparison of these values with those from table 2 we can see that by DCF degradation on the studied anodic compositions the breaking of the aromatic rings and the partial mineralization of formed by-products took place.

This process proceeded with better yields for Ti/RuO_2-TiO_2. For $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 the mineralization in small extent for 50 mg/L DCF by comparison with the other working concentrations takes place and this is in contrast with homogeneous results determined for TOC removal using Ti/RuO_2-TiO_2, despite of DCF initial concentration. It appears for this concentration of $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 the process of by-products formation was more intense than their mineralization.

Conclusions

This paper investigated the degradation of DCF at two compositions of dimensionally stable anodes, namely Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2.

The investigation of UV spectra and TOC removal showed the effectiveness of dimensionally stable anodes towards advanced degradation of DCF, a non-biodegradable micro pollutant. Along with the degradation also a mineralization process occurred.

For both anodic compositions the best results for the mineralization of DCF (40-44%), for all studied concentrations, were obtained at 300 A/m^2 at 120 min of electrolysis.

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