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TECHNICAL FACULTY „MIHAILO PUPIN“
ZRENJANIN, REPUBLIC OF SERBIA

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Proceedings

URBAN ECO conference 2014

4th INTERNATIONAL CONFERENCE

"ECOLOGY OF URBAN AREAS 2014"

Zrenjanin, october 9-10, 2014.
Serbia

IV International Conference
„ECOLOGY OF URBAN AREAS" 2014

DEGRADATION OF PIROXICAM BY ELECTROCHEMICAL OXIDATION AT DSA ELECTRODES

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ABSTRACT

The presence of pharmaceuticals in water is undesirable because of their adverse effects on aquatic organisms even in concentration of ng-μg/L. This paper dealt with the degradation of piroxicam (PXC), a nonsteroidal anti-inflammatory drug (NSAID), by electrochemical oxidation at dimensionally stable anodes (DSA). Two compositions of DSA were used: Ti/RuO2-TiO2 and Ti/RuO2/SnO2-Sb2O5-RuO2. Current densities of 200 and 300 A/m2 were applied for electrolyses time of 60, 120 and 180 minutes in neutral or basic medium. The ultraviolet (UV) spectra of the electrolysed solutions were recorded and total organic carbon (TOC) analyses were carried out to assess the degradation process. The most effective in degradation of PXC was the anodic composition Ti/RuO2-TiO2 in basic medium.

Key words: *degradation, dimensionally stable anodes, electrochemical oxidation, piroxicam.*

INTRODUCTION

Pharmaceuticals are used at large scale and their diversity increases yearly. They are a new class of emerging micropollutants and the concern regarding their presence in water is due to adverse effects towards aquatic organisms even at very low concentration. Pharmaceuticals pass almost unchanged through wastewater treatment plants. Thus, pharmaceuticals enter the water bodies through effluent discharge into aquatic ecosystems where may reach concentrations from ng/L to μg/L (Corcoll et al., 2014).

As a consequence it is strongly necessary to find new ways to remove the pharmaceuticals from wastewaters. Electrochemical technologies are very promising because of their advantages: (a) electrons are clean reagents; (b) effective control of the electron transfer rate (current density); (c) measurement of reaction conditions (current density and electrode potential); (d) the process can be turned on and off via the current; (e) can often use benign (e.g., ambient) conditions of temperature and pressure (Walsh, 2001).

The aim of this paper was the pharmaceuticals degradation by electrochemical oxidation at dimensionally stable anodes (DSA) in order to obtain effluents compatible with the environment. Piroxicam (PXC), a nonsteroidal anti-inflammatory drug, was chosen as model of pharmaceuticals.

THEORY

The areas of application for the electrochemical methods are the pretreatment of biorefractory organic pollutants and the removal of pollutants present at low levels of concentration (in which case traditional methods are affected by slow kinetics) (De Francesco and Costamagna, 2004).

The electrochemical techniques for wastewater treatment also involve electrochemical oxidation (Sires and Brillas, 2012). The electrochemical oxidation provides either the removal of biorefractory organic

pollutants or can induce the biodegradability (Martínez-Huitle et al., 2004) and consequently it can be integrated as advanced treatment stage in conventional wastewater treatment schemes.

In this paper the degradation of biorefractory organic pollutants from wastewaters by electrochemical oxidation at DSA is approached. DSA are electrode materials that consist of a layer of conductive metal oxides with electrocatalytic properties deposited on titanium substrate. The introduction of the catalytic reaction in the electrochemical technology, known as electrocatalytic technology, not only causes a significant increase of the efficiency but increases the availability for biorefractory organic pollutants.

The active oxides of DSA are not absolutely the best electrocatalysts, but they are exceptional in terms of their versatility. Transition metal oxides are among the most versatile ever known electrocatalysts (Trasatti, 2000). Titanium, due to the excellent combination of mechanical properties, low density and resistance to corrosion is generally the most used substrate.

Initially designed for the clor-alkali industry, DSA are increasingly studied as electrode material for the electrochemical oxidation of organics. Among the compounds degraded by DSA or modified DSA in the papers are reported dyes (Basiri Parsa et al., 2013; Tavares et al., 2012) or textile effluents (Basha et al., 2012), herbicides (Aquino Neto et al., 2009; Zaviska et al., 2011), 2,4- dichlorophenol (Niu et al., 2013), nitrophenols (Adams et al., 2009) or pharmaceuticals active compounds (Santos et al., 2013).

METHODS

The degradation of PXC by electrochemical oxidation was carried out in a Plexiglas cell. Two DSA anodes and three stainless steel cathodes were used at 1 cm gap. Active surface area was 38 cm2. Experiments were carried out by applying current densities of 200 and 300 A/m2 at 60, 120 and 180 minutes of electrolysis and values of pH: 7 and 10, respectively.

The DSA electrodes had the compositions Ti/RuO2-TiO2 (molar ratio in the precursors solution 30:70) and Ti/RuO2/SnO2-Sb2O5-RuO2 (molar ratio in the precursors solution 94:3:3) and they were prepared by thermal decomposition of appropriate precursors. The DSA electrodes preparation was presented previously (Ihos et al., 2009; Ihos et al., 2011) with the notice that for Ti/RuO2/SnO2-Sb2O5-RuO2 in the mixture of the precursors was also introduced the precursor RuCl3.nH2O (Fluka). Electrolyses were carried out in solutions of 50 mg/L and 200 mg/L PXC, respectively. The supporting electrolyte was 0.1 M Na2SO4. PXC (4-hydroxy-2-methyl-N-(2-pyridyl)-2H-1,2-benzothiazin-3-caboxyamid-1,1-dioxid) was produced by Nantong Jinghua Pharmaceutical Co. Ltd. The Na2SO4 and NaOH were supplied by Merck and they were reagent grade. The solutions were prepared with distilled water.

The process was followed by recording the UV spectra by using a Specord 205 - Analytik Jena spectrophotometer controlled by computer. TOC was monitored by a TOC analyzer (Shimadzu - TOC-VCPH) computer controlled.

FINDINGS

Fig. 1 shows the chemical structure of the PXC. In Fig. 2 are presented the UV spectra of PXC in 0.1 M Na2SO4 and of the electrolyzed solutions at various electrolysis time. The shape of spectra recorded for other concentration PXC and working conditions and is analogous to those presented in Fig. 2.

The maxima of absorbance of PXC are characteristic to benzene, pyridine and naphthalene derivates: a. ethylene bands with maxima at 193 and 206 nm, that overlap with that of sodium sulphate; b. bands of benzene, pyridine and thia-9-aza-bicycle rings at 253, 274, 280 nm; c. bands due to substituents and condensed ring at 357 and 363 nm [Balaban et al., 1983).

Tables 1-4 shows the UV absorbance bands evolution depending on PXC degradation. Based on data listed in Tables 1-4, the efficiencies of absorbance decrease were calculated corresponding to evolution of absorbance maxima depending on working conditions. These efficiencies are shown in Tables 5-8.

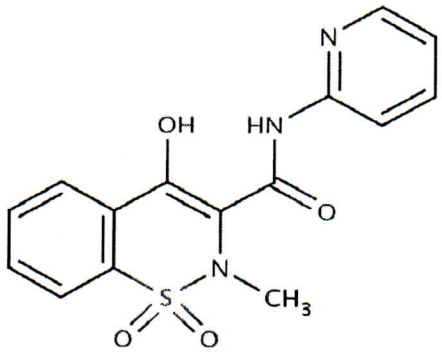

Figure 1. Chemical structure of PXC

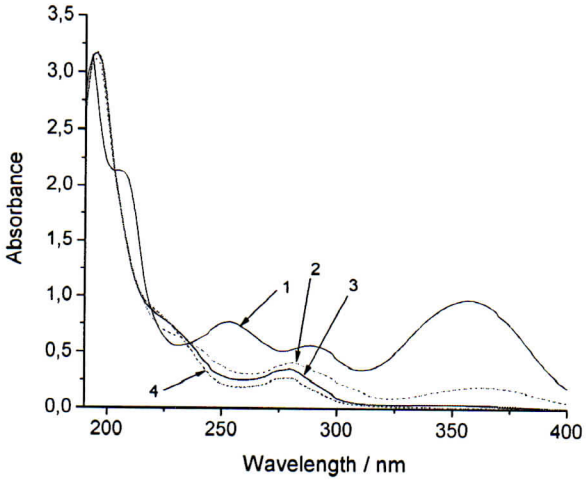

Figure 2. UV spectra of PXC in 0.1 M Na_2SO_4 anode: Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2; c_{ini}= 50 mg/L PXC; pH_{ini}: 7;current density: 200 A/m^2; 1-0 min; 2-60 min; 3-120 min; 4-180 min

Table 1: UV absorbance evolution during the degradation process of PXC at Ti/RuO2-TiO2 anodes and initial pH of 7

Anodic composition/ pHini	PXC concen tration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance							
				193	206	253	274	280	288	357	363
			0	2.31	2.11	0.77	0.52	0.52	0.55	0.99	0.94
		200	60	2.87	1.68	0.38	0.41	0.45	0.39	0.20	0.21
			120	2.92	1.66	0.31	0.40	0.43	0.32	0.01	0.01
			180	2.87	1.63	0.25	0.34	0.36	0.25	0	0
	200		0	2.31	2.11	0.77	0.52	0.52	0.55	0.99	0.94
		300	60	2.91	1.69	0.37	0.42	0.44	0.36	0.15	0.15
Ti/RuO2-			120	2.92	1.65	0.24	0.31	0.33	0.23	0.01	0.01
TiO2 /			180	2.90	1.68	0.16	0.21	0.22	0.13	0	0
7			0	3.07	2.12	0.76	0.51	0.51	0.55	0.97	0.94
		200	60	3.15	1.75	0.31	0.37	0.41	0.37	0.13	0.14
			120	3.13	1.76	0.21	0.29	0.36	0.34	0.02	0.02
	50		180	3.15	1.73	0.22	0.30	0.31	0.21	0	0
			0	3.07	2.12	0.76	0.51	0.51	0.55	0.97	0.94
		300	60	3.12	1.70	0.32	0.38	0.40	0.31	0.09	0.09
			120	3.10	1.70	0.15	0.21	0.24	0.20	0	0
			180	3.07	1.70	0.12	0.17	0.17	0.09	0	0

Table 2: UV absorbance evolution during the degradation process of PXC at Ti/RuO2-TiO2 anodes and initial pH of 10

Anodic composition/ pHini	PXC concen tration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance						
				193	206	253	274	280	288	355
			0	2.34	2.15	0.77	0.53	0.53	0.58	0.95
		200	60	2.91	1.75	0.42	0.46	0.49	0.40	0.19
			120	2.98	1.70	0.29	0.38	0.42	0.33	0,03
			180	2.94	1.66	0.25	0.33	0.35	0.24	0
	200		0	2.34	2.15	0.77	0.53	0.53	0.58	0.95
		300	60	2.87	1.63	0.33	0.37	0.38	0,31	0.14
			120	2.89	1.63	0.19	0.25	0.26	0.17	0.01
Ti/RuO2-			180	2.85	1.63	0.12	0.17	0.17	0.09	0
TiO2 / 10			0	3.15	2.19	0.76	0.52	0.53	0.58	0.92
		200	60	3.17	1.80	0.39	0.45	0.48	0.38	0.15
			120	3.14	1.75	0.20	0.28	0.34	0.32	0
	50		180	3.10	1.74	0.19	0.26	0.28	0.21	0
			0	3.15	2.19	0.76	0.52	0.53	0.58	0.92
		300	60	3.12	1.68	0.31	0.35	0.37	0.28	0.10
			120	3.08	1.68	0.17	0.23	0.24	0.15	0
			180	3.15	1.78	0.11	0.15	0.15	0.07	0.01

Table 3: UV absorbance evolution during the degradation process of PXC at Ti/RuO2/SnO2- Sb2O5-RuO2 anodes and and initial pH of 7

Anodic composition/ pHini	PXC concen tration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance							
				193	197	206	253	280	288	357	363
			0	2.31	2.08	2.11	0.77	0.52	0.55	0.99	0.94
		200	60	2.86	2.64	1.68	0.40	0.49	0.39	0.15	0.14
			120	2.91	2.80	1.73	0.27	0.41	0.38	0.04	0.04
			180	2.94	2.78	1.67	0.28	0.38	0.27	0.01	0.01
	200		0	2.31	2.08	2.11	0.77	0.52	0.55	0.99	0.94
		300	60	2.87	2.64	1.67	0.38	0.46	0.37	0.16	0.15
Ti/RuO2/SnO2-			120	2.93	2.76	1.64	0.28	0.37	0.27	0.02	0.02
Sb2O5-RuO2/			180	2.91	2.75	1.64	0.21	0.28	0.19	0.01	0.01
7			0	3.07	2.49	2.12	0.76	0.51	0.55	0.97	0.94
		200	60	3.10	3.00	1.71	0.34	0.41	0.35	0.19	0.19
			120	3.17	3.08	1.71	0.26	0.35	0.25	0.03	0.02
	50		180	3.18	3.10	1.72	0.20	0.27	0.18	0.01	0
			0	3.07	2.49	2.12	0.76	0.51	0.55	0.97	0.94
		300	60	3.13	3.02	1.70	0.31	0.38	0.31	0.13	0.13
			120	3.08	2.95	1.63	0.16	0.25	0.21	0.01	0.01
			180	3.08	2,90	1,57	0.14	0.19	0.11	0	0

Table 4: UV absorbance evolution during the degradation process of PXC at Ti/RuO2/SnO2- Sb2O5-RuO2 anodes and and initial pH of 10

Anodic composition/ pHini	PXC concen tration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance						
				193	196	206	253	280	288	355
			0	2.34	2.10	2.15	0.77	0.53	0.58	0.95
		200	60	2.67	2.51	1.51	0.37	0.43	0.34	0.18
			120	2.98	2.92	1.76	0.37	0.47	0.36	0.09
			180	2.92	2.88	1.68	0.29	0.39	0.28	0.02
	200		0	2.34	2.10	2.15	0.77	0.53	0.58	0.95
		300	60	2.80	2.69	1.63	0.37	0.44	0.35	0.14
Ti/RuO2/SnO2-			120	2.92	2.86	1.66	0.30	0.39	0.29	0.04
Sb2O5-RuO2/			180	2.92	2.82	1.63	0.23	0.30	0.20	0.01
10			0	3.15	2.68	2.19	0.76	0.53	0.58	0.92
		200	60	3.18	3.14	1.79	0.37	0.45	0.36	0.14
			120	3.14	3.07	1.65	0.27	0.37	0.27	0.02
	50		180	3.10	3.10	1.63	0.21	0.29	0.20	0
			0	3.15	2.68	2.19	0.76	0.53	0.58	0.92
		300	60	3.11	3.07	1.70	0.34	0.42	0.33	0.11
			120	3.11	3.06	1.58	0.20	0.27	0.19	0.01
			180	3.08	3.03	1.59	0.16	0.21	0.13	0

Table 5: Absorbance peak abatement efficiency during the degradation process of PXC at Ti/RuO2-TiO2 anodes and and initial pH of 7

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance abatement efficiency [%]			
				206	253	288	357
			60	20.37	50.64	29.09	79.79
		200	120	21.32	59.74	41.81	98.98
	200		180	22.74	67.53	54.54	100
			60	19.90	51.94	34.54	84.84
		300	120	21.80	68.83	58.18	98.98
Ti/RuO2- TiO2			180	20.37	79.22	76.36	100
/7			60	17.45	59.21	32.72	86.59
		200	120	16.98	72.36	38.18	97.93
	50		180	18.39	71.05	61.81	100
			60	19.81	57.89	43.63	90.72
		300	120	19.81	80.26	63.63	100
			180	19.81	84.21	83.63	100

Table 6: Absorbance peak abatement efficiency during the degradation process of PXC at Ti/RuO2-TiO2 anode and and initial pH of 10

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance abatement efficiency [%]			
				206	253	288	355
			60	18.60	45.45	31.03	80.00
		200	120	20.93	62.33	43.10	96.84
	200		180	22.79	67.53	58.62	100.00
			60	24.19	57.14	46.55	85.26
		300	120	24.19	75.32	70.69	98.95
Ti/RuO2-TiO2 /			180	24.19	84.42	84.48	100.00
10			60	17.81	48.68	34.48	83.70
		200	120	20.09	73.68	44.83	100.00
	50		180	20.55	75000	63.79	100.00
			60	23.29	59.21	51.72	89.13
		300	120	23.29	77.63	74.14	100.00
			180	18.72	85.53	87.93	100.00

Table 7: Absorbance peak abatement efficiency during the degradation process of PXC at Ti/RuO2/SnO2- Sb2O5-RuO2 and and initial pH of 7

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance abatement efficiency [%]			
				206	253	288	357
			60	20.38	48.05	29.09	84.85
		200	120	18.01	64.94	30.91	95.96
	200		180	20.85	63.64	50.91	98.99
			60	20.85	50.65	32.73	83.84
		300	120	22.27	63.64	50.91	97.98
Ti/RuO2/SnO2-			180	22.27	72.73	65.45	98.99
Sb2O5-RuO2/			60	19.34	55.26	36.36	80.41
7		200	120	19.34	65.79	54.55	96.91
	50		180	18.87	73.68	67.27	98.97
			60	19.81	59.21	43.64	86.60
		300	120	23.11	78.95	61.82	98.97
			180	25.94	81.58	80.00	100.00

Table 8: Absorbance peak abatement efficiency during the degradation process of PXC at Ti/RuO2/SnO2-Sb2O5-RuO2 and and initial pH of 10

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance abatement efficiency [%]			
				206	253	288	355
			60	29.77	51.95	41.38	81.05
		200	120	18.14	51.95	37.93	90.53
	200		180	21.86	62.34	51.72	97.89
			60	24.19	51.95	39.66	85.26
		300	120	22.79	61.04	50.00	95.79
Ti/RuO2/SnO2-			180	24.19	70.13	65.52	98.95
Sb2O5-RuO2/			60	18.26	51.32	37.93	84.78
10		200	120	24.66	64.47	53.45	97.83
	50		180	25.57	72.37	65.52	100.00
			60	22.37	55.26	43.10	88.04
		300	120	27.85	73.68	67.24	98.91
			180	27.40	78.95	77.59	100.00

Table 9: TOC evolution during the degradation process of PXC at DSA electrodes electrolysis time: 180 min; TOC of 200 mg/L PXC: 3,81 mg C/L (dil. 1:25); TOC of 50 mg/L PXC: 1,01 mg C/L (dil. 1:25)

PXC concentration [mg/L]	pHini	Anodic composition	Current density [A/m2]	TOC [mg C/L]	TOC abatement efficiency [%]
		Ti/RuO2-TiO2	200	3.420	10.24
200	7		300	3.090	18.90
		Ti/RuO2/SnO2- Sb2O5-RuO2	200	3.570	6.30
			300	3.480	8.66
		Ti/RuO2-TiO2	200	3.340	12.33
200	10		300	2.865	24.80
		Ti/RuO2/SnO2- Sb2O5-RuO2	200	3.200	16.00
			300	3.160	17.07
		Ti/RuO2-TiO2	200	0.837	17.12
50	7		300	0.585	42.07
		Ti/RuO2/SnO2- Sb2O5-RuO2	200	0.881	12.77
			300	0.823	18.51
		Ti/RuO2-TiO2	200	0.740	26.73
50	10		300	0.489	51.58
		Ti/RuO2/SnO2- Sb2O5-RuO2	200	0.887	12.18
			300	0.715	29.21

DISCUSSION

In case of anodic compositions Ti/RuO2-TiO2, at neutral pH it can be observed a low reduction of absorbance at 206 nm as the electrolysis time increased, regardless of the applied current density and the initial concentration of the solution. Thus, the efficiency of absorbance decrease at 206 nm ranged from 20-23% for 200 mg/L PXC and 17-20% for 50 mg/L.

The situation is different for the other wavelengths. Thus, important decreases of the absorbance as the electrolysis time and current density increased were recorded regardless the initial concentration of

solution. The best efficiencies of the absorbance decrease were recorded at 357 nm (that practically disappeared from the spectrum), followed by that at 253 nm and 288 nm, respectively. This behaviour could suggest that the structure of the benzene ring was not significantly affected, while the pyridine ring and adjacent substituents to the aromatic ring are degraded with higher efficiencies.

The above findings are valid both for Ti/RuO2-TiO2 anodes and Ti/RuO2/SnO2-Sb2O5-RuO2, both in neutral medium and basic medium. It can be noticed that the best results for both working concentrations were recorded at a current density of 300 A/m2 and 180 minute of electrolysis.

By comparing efficiencies of the absorbance decrease for anodic composition Ti/RuO2-TiO2 in neutral and basic medium it is revealed the absorbance decrease was more significant regardless of the initial concentration.

Not the same aspects were observed for the anodic composition Ti/RuO2/SnO2-Sb2O5-RuO2. Thus, at 206 nm the decrease was higher in basic medium regardless of solution initial concentration, at 253 nm it was higher in neutral medium regardless of solution initial concentration, at 288 nm they were almost the same in neutral and basic medium for the initial concentration of 200 mg/L PXC and higher in neutral medium for the initial concentration of 50 mg/L PXC, and at 357 nm they were almost de same regardless of pH and initial concentration.

TOC analyses were carried out for the electrolyzed solutions. The results are tabulated as follows. It can be noticed a good correlation between the electrochemical degradation and TOC evolution.

The survey of data listed in Table 9 revealed that the advanced degradation of the pollutant occurred with higher efficiencies both in neutral and basic medium for both initial concentrations of the solutions for anodic composition Ti/RuO2-TiO2 as compared with Ti/RuO2/SnO2- Sb2O5-RuO2.

For the anodic composition Ti/RuO2-TiO2, the highest TOC removal efficiencies were recorded in basic medium for both solution initial concentrations. The same behaviour was observed for the anodic composition Ti/RuO2/SnO2- Sb2O5-RuO2.

CONCLUSIONS AND IMPLICATIONS

UV spectra survey revealed a complex degradation process that could be explained by oxidation and bond cleavage between the pyridine and condensed rings, as well as their oxidation. The appearance of new maxima in spectra confirmed the advanced oxidation of PXC.

Based on absorbance abatement efficiencies at wavelength corresponding to absorbance maxima, it can be assumed that the structure of the benzene ring was poorly affected, while the pyridine ring and the adjacent substituents of aromatic ring were degraded with higher efficiencies. The efficiencies of the absorbance decrease corresponding to maxima were higher in basic medium almost in all situations.

Regardless the solution initial concentration, the best removal TOC efficiency was recorded in basic medium for both anodic compositions. The most effective proved to be the anodic composition Ti/RuO2-TiO2 with TOC removal efficiency of 51.58%.

Current facilities do not provide the removal of biorefractory organic pollutants from wastewater treatment and therefore it is necessary to find solutions to provide effluents that meet the conditions of discharge specified by regulations in use.

The research presented in this paper is part of the current concerns existing at European level for providing and developing methods for the treatment of biorefractory organic pollutants effluents so that their transformation into compounds that do not endanger the natural habitat is accomplished.