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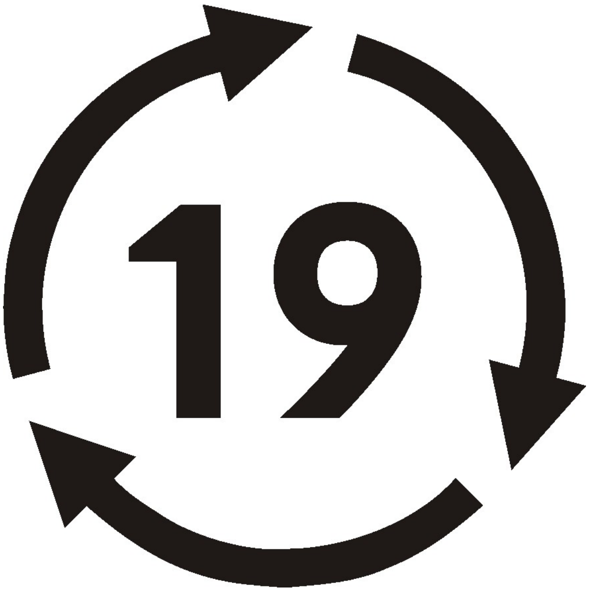

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DSA ELECTRODES INVOLVEMENT IN PHOTOCATALYTICALLY-ASSISTED ELECTROCHEMICAL DEGRADATION OF IBUPROFEN

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ABSTRACT

The photocatalytically-assisted electrochemical degradation of ibuprofen (IBP) in basic medium was carried by using Dimensionally Stable Anodes (DSA) with the composition Ti/RuO_2-TiO_2 and Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2, and zeolite-supported TiO_2 based on (Z-TiO_2-Ag and Z2-TiO_2) photocatalysts. Also photoelectrochemical experiments were carried out for assessment of photocatalysts contribution to IBP degradation. The experiments were carried out by applying current densities of 200 and 300 A/m^2 simultaneously with UV irradiation for 60, 120 and 180 minutes, and concentration of the photocatalysts of 1 g/L. The degradation processes were monitored by recording the UV spectra and determination of Total Organic Carbon (TOC). The best result for TOC removal efficiency was of 44.27% and it was registered in the photocatalytically-assisted electrochemical degradation of IBP on Ti/RuO_2-TiO_2 anodes and Z2-TiO_2 photocatalyst at 300 A/m^2 and 180 min of process duration.

INTRODUCTION

The pharmaceutically active compounds are designed to have biological effects and they have a great variability of chemical structures, and also they underwent variations in time regarding the concentration [1, 2].

Continuous progress effectuated within the analytical equipments and methodologies field allow the pharmaceuticals detection at low levels of concentration in different environmental matrices [3,4].

Studies have reported the presence of pharmaceuticals at low levels of concentration (ng-µg/L) in the surface waters and that proved unambiguity that their removal in the water treatment plants is incomplete [5]. Pharmaceuticals could have deleterious effects on aquatic organisms even emerging in the environment at low level of concentration [6,7].

Therefore it is necessary to find solutions for the advanced treatment of pharmaceuticals effluents that contain biorefractory pharmaceutically active compounds. The application of electrochemical process and photocatalysis is a viable choice to achieve this challenge [8,9].

The aim of this paper was to assess the degradation of ibuprofen (IBP), a non-steroidal anti-inflammatory drug, by photocatalytically-assisted electrochemical process by using Dimensionally Stable Anodes (DSA), Ti/RuO_2-TiO_2 and Ti/RuO_2/SnO_2–Sb_2O_5-RuO_2, and zeolite-supported TiO_2 based on (Z-TiO_2-Ag and Z2-TiO_2) photocatalysts. Also, photoelectrochemical experiments were carried out to determinate the contribution of the photocatalysts on pollutant degradation.

MATERIALS and METHODS

IBP [2-(4-isobutylphenyl) propanoic acid] was supplied by BASF, and by Merck the Na_2SO_4 and NaOH. Distilled water was used for the preparation of the solutions. The working solutions were of 50 mg/L in 0.1 M Na_2SO_4, 100 mL and pH 11.

The DSA anodes used were Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2$–Sb_2O_5-RuO_2. The anodes were prepared by thermal decomposition of appropriate precursors.

The photocatalysts were zeolite-supported TiO_2 based on (Z-TiO_2-Ag and Z2-TiO_2)

The photocatalytically-assisted electrochemical degradation of IBP was 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 200 and 300 A/m^2 at electrolysis time of 60, 120 and 180 minutes. The concentration of the photocatalysts was 1 g/L in any experiments and they were kept in suspension by using a magnetic stirrer. The radiation source was a lamp UVP: 254 nm UV, 8-Watt, 230 V~50Hz and 0.32 Amps.

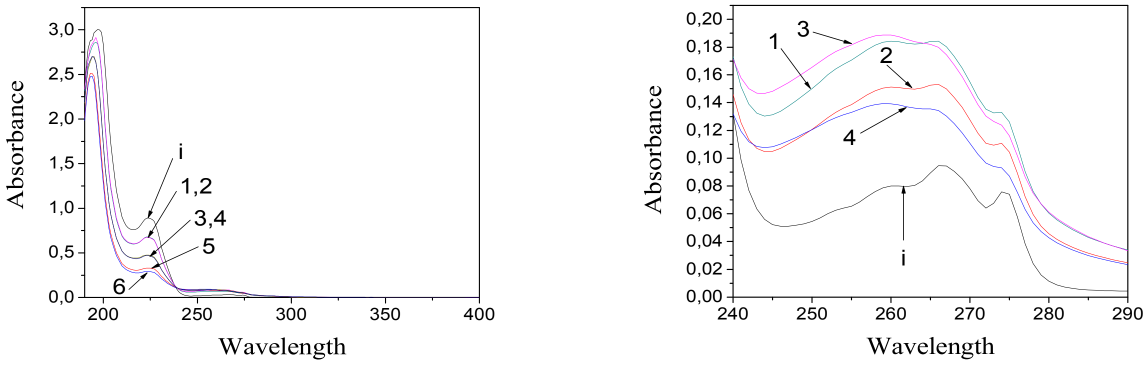
The photoelectrochemical experiments were carried out in the same conditions as the photocatalytically-assisted electrochemical ones with one difference, namely the absence of the photocatalyst.

The samples underwent centrifugation at 5000 rpm and 20 minutes. A Specord 205 - Analytic Jena spectrophotometer controlled by computer recorded the UV spectra. TOC was monitored by a TOC analyzer (Shimadzu - TOC-VCPH) computer controlled.

RESULTS

As it was presented previously [10], the UV spectrum of the IBP in 0.1 M Na_2SO_4 displayed absorbance peaks at 196 nm (assigned to methyl groups), 223 nm (assigned to acidic group), and absorbance peaks of low values 258, 267 and 273 nm (all assigned to benzenic ring and changes induced by propanoic acid and methylpropyl group).

The oxidative process, regardless of DSA anodic composition, photocatalyst and current density, was reflected by the abatement of the absorbance peaks from 196 and 223 nm and the increase of those from 258, 267 and 273 nm (Figs.1 and 2) both for the photocatalytically-assisted electrochemical degradation and the photoelectrochemical one, the findings presented previously [10] for the electrochemical degradation remaining valid.



Figs. 1 and 2. UV spectra of IBP in 0.1 M Na_2SO_4
photocatalytically-assisted electrochemical degradation (a) and photoelectrochemical degradation (b)

UV range: 190-400 nm; anode: Ti/RuO_2-TiO_2;
c_{ini}= 50 mg/L IBP; pH_{ini}: 11;
current density: 300 A/m^2; photocatalyst: Z-TiO_2-Ag
i-0 min; 1-60 min (a); 2-60 min (b);
3-120 min (a); 4-120 min (b);
5-180 min (a); 6-180 min (b)

UV range: 240 – 290 nm; anode:
$Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2; c_{ini}= 50 mg/L IBP;
pH_{ini}: 11; current density: 200 A/m^2;
photocatalyst: Z2-TiO_2
i-0 min; 1-60 min (a); 2-60 min (b);
3-120 min (a); 4-120 min (b)

The process efficiency in photocatalytically-assisted electrochemical degradation and electrochemical degradation are shown in Tables 1 and 2.

The contribution of Z-TiO_2-Ag photocatalyst to TOC removal efficiency on Ti/RuO_2-TiO_2 anodes was low: 1,32% (200 A/m^2, 120 min), 6,8% (300 A/m^2, 120 min) şi 2,87% (300 A/m^2, 180 min), while the contribution of Z-TiO_2 photocatalyst was of 10.16% at 300 A/m^2 and 180 min (see Table 1).

The data listed in Table 2 revealed that the presence of Z-TiO_2-Ag photocatalyst in the same system with Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 anodes did not lead to TOC removal efficiency increase; on the contrary, the photocatalytically-assisted electrochemical degradation was impeded by its presence. The photocatalytically-assisted electrochemical degradation on Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 and Z2-TiO_2 was not favoured by the increase of current density and electrolysis time. The contribution of the photocatalyst to TOC removal efficiency increase at 120 min of photocatalytically-assisted electrochemical degradation and current densities of 200 and 300 A/m^2 was 14.09% and 11.22%, respectively.

Table 1. Working conditions and TOC evolution in photocatalytically-assisted electrochemical degradation and photoelectrochemical degradation of IBP on Ti/RuO_2-TiO_2

c_{ini}=50 mg/L IBP in Na_2SO_4 0.1 M; TOC_{ini} = 51.45 mg C/L; photocatalysts: Z-TiO_2-Ag and Z2-TiO_2

Degradation	Current density / A/m^2	Time / min	Z-TiO_2-Ag	Z2-TiO_2
			TOC removal efficiency / %	TOC removal efficiency / %
photocatalytically-assisted electrochemical	200	120	13.85	23.09
photoelectrochemical	200	120	20.17	20.17
photocatalytically -assisted electrochemical	300	120	28.66	27.50
photoelectrochemical	300	120	24.68	24.68
photocatalytically -assisted electrochemical	300	180	36.98	44.27
photoelectrochemical	300	180	34.11	34.11

Table 2. Working conditions and TOC evolution in photocatalytically-assisted electrochemical degradation of IBP on Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2

c_{ini}=50 mg/L IBP in Na_2SO_4 0.1 M; TOC_{ini} = 51.45 mg C/L; photocatalysts: Z-TiO_2-Ag and Z2-TiO_2

Degradation	Current density / A/m^2	Time/ min	Z-TiO_2-Ag	Z2-TiO_2
			TOC removal efficiency / %	TOC removal efficiency / %
photocatalytically-assisted electrochemical	200	120	17.90	33.10
photoelectrochemical	200	120	19.01	19.01
photocatalytically-assisted electrochemical	300	120	18.46	30.61
photoelectrochemical	300	120	19.39	19.39
photocatalytically-assisted electrochemical	300	180	34.07	26.20
photoelectrochemical	300	180	34.88	34.88

CONCLUSIONS

The photocatalytically-assisted electrochemical de gradation of IBP in basic medium by using DSA anodes, Ti/RuO_2-TiO_2 and Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2, and zeolite-supported TiO_2 based on photocatalysts, Z-TiO_2-Ag and Z2-TiO_2, revealed their contribution in TOC removal efficiency.
The most effective photocatalyst was Z2-TiO_2 regardless of anodic composition. The behaviour of Z2-TiO_2 photocatalyst with respect to anodic compositions was different. Thus, in the case of Ti/RuO_2-TiO_2 anodes the contribution of the photocatalyst was higher at the highest value of current density and reaction time: contribution to TOC abatement of 10.16% at 300 A/m^2 and 180 min, while for Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 the contribution of the photocatalyst was higher at the lowest value of current density and reaction time: contribution to TOC abatement of 14.09% at 200 A/m^2 and 120 min of process duration.

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