

PROCEEDINGS OF

**THE INTERNATIONAL SYMPOSIUM
ON ANALYTICAL AND ENVIRONMENTAL
PROBLEMS, WITH SPECIAL EMPHASIS
ON HEAVY METAL IONS AS CONTAMINANTS**

24 September 2012

Edited by
Zoltán Galbács

18.



**SZAB
SZEGED, HUNGARY**

**THE 18th INTERNATIONAL SYMPOSIUM ON ANALYTICAL
AND ENVIRONMENTAL PROBLEMS, WITH SPECIAL
EMPHASIS ON HEAVY METAL IONS AS CONTAMINANTS**

Organised by

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ISBN 978-963-306-165-7

Financial support from the European Union's European Regional
Development Fund, provided within the frameworks of the
Hungary-Romania Cross-Border Cooperation Programme 2007-2013, under
project No. HURO/1001/232/2.2.2. (METCAP) is kindly acknowledged.

NON-STEROIDAL ANTI-INFLAMMATORY DRUGS DEGRADATION BY ELECTROCHEMICAL METHODS

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ABSTRACT

Ibuprofen (IBP) was chosen as a model for non-steroidal anti-inflammatory drugs and its degradation in aqueous solution was carried out by electrochemical oxidation on Dimensionally Stable Anodes (DSA). The DSA had the compositions: Ti/RuO₂-TiO₂ and Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂. The electrolyses were carried in basic medium by using solutions of IBP or IBP and sodium carboxymethyl cellulose (CMC) in 0.1 M Na₂SO₄ supporting electrolyte. The removal of IBP was assessed by recording UV spectra and total organic carbon (TOC) or chemical oxygen demand (COD) of the electrolysed solutions. The results showed the effectiveness of DSA in IBP degradation in aqueous solutions both in the matrix that contains only IBP and those containing also CMC.

INTRODUCTION

Nowadays pharmaceuticals represent a novel class of micropollutants that have raised concerns because their presence in the environment could constitute a potential risk for aquatic organisms [1-4].

Because the pharmaceuticals pass through the sewage treatment plants mostly unchanged and they have been detected as emerging pollutants in surface waters. The concentrations ranged from ng/L to µg/L [5, 6].

As a logical consequence, it is important to treat wastewaters from pharmaceutical manufacturing industry drugs before the discharge in the sewerage systems. In this way, the biodegradability of pharmaceuticals effluents will be induced or the pharmaceuticals will be removed before they reach the waste treatment plants.

Several processes were applied to abate the organic load of pharmaceutical effluents, such as: photocatalysis [7,8], adsorption [9] and ultrasonic irradiation [10].

The aim of this paper was to assess the degradation of ibuprofen (IBP), a non-steroidal anti-inflammatory drug, by electrochemical oxidation on Dimensionally Stable Anodes (DSA). The experiments were carried out in aqueous solutions in basic medium. One series of the experiments were carried out in solutions that contained only IBP and another series contained IBP and sodium carboxymethyl cellulose (CMC). The second series of experiments was carried out to envisage the application of electrochemical oxidation to pharmaceuticals effluents treatment, CMC being one of the excipients for IBP containing drugs pharmaceutical formulation.

MATERIALS and METHODS

The DSA electrodes used in these experiments were Ti/RuO₂-TiO₂ and Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂. The electrodes were prepared by thermal decomposition of appropriate precursors.

IBP [2-(4-isobutylphenyl)propanoic acid] was supplied by BASF, CMC by a local company, and by Merck the sodium sulphate and sodium hydroxide. Distilled water was used for the preparation of the solutions. The pH of the working solutions was 11.

The electrolyses were accomplished by using two DSA anodes and three stainless steel cathodes 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 electrolysis time of 180 minutes. Electrolyses were carried out in solutions of 50 mg/L IBP, and solutions of 50 mg/L IBP and 820 mg/L CMC. The supporting electrolyte was 0.1 M Na₂SO₄.

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. COD was determined according to the Romanian standard SR ISO 6060/1996.

RESULTS

The spectrum of IBP in 0.1 M Na₂SO₄ recorded in UV range is shown in Figs.1 and 2.

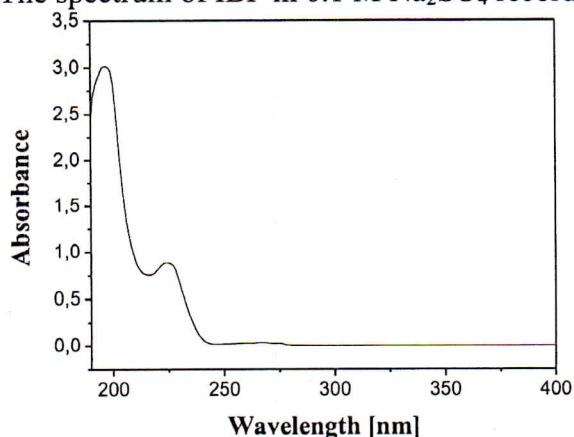


Fig.1. UV spectrum of IBP in 0.1 M Na₂SO₄ dil. 1:2.5

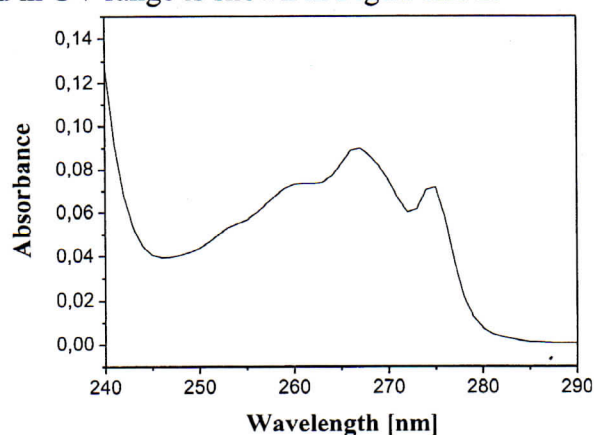


Fig.2. UV spectrum of IBP in 0.1 M Na₂SO₄; UV range: 240-290 nm

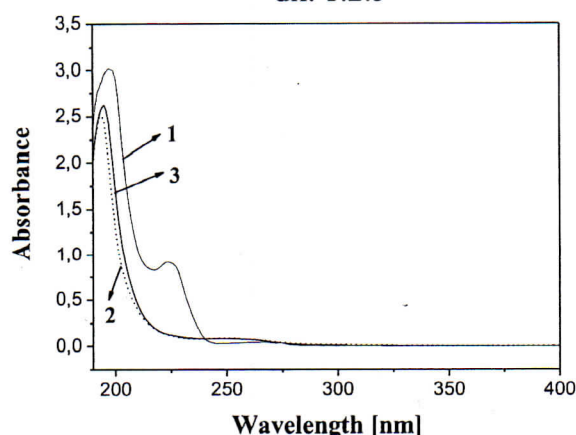


Fig.3. UV spectra of IBP-CMC in 0.1 M Na₂SO₄ dil. 1:2.5

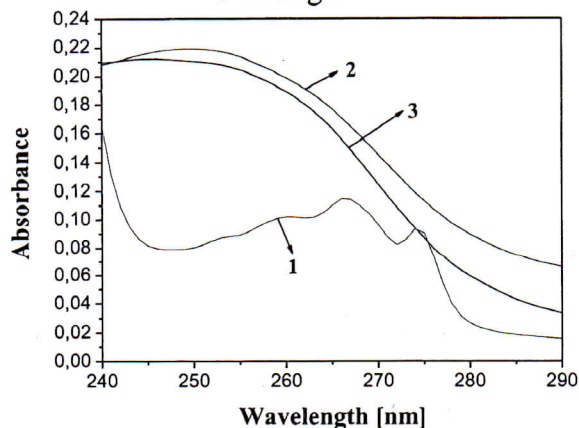


Fig.4. UV spectra of IBP-CMC in 0.1 M Na₂SO₄ UV range: 240-290 nm

$c_{ini} = 50$ mg/L IBP and 820 mg/L CMC; $pH_{ini} = 11$; current density: 300 A/m²; electrolysis time: 180 min;
1. IBP-CMC_{ini}; 2. anode: Ti/RuO₂-TiO₂; 3. Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂

The UV spectrum of the IBP in 0.1 M Na₂SO₄ displayed three absorptions bands in the range 190-280 nm. The more intense band with the absorbance peak at 196 nm can be assigned to methyl groups and the second one with the absorbance peak at 223 nm to acidic group (Fig.1).

The band ranged between 250 - 280 nm corresponding to aromatic ring exhibited low values of the absorbance peaks. The absorbance peaks at 258, 267 and 273 nm can be assigned to benzenic ring and changes induced by propanoic acid and methylpropyl group (Fig. 2). The absorbance peaks variation during the electrochemical degradation of IBP on the two compositions of DSA is shown in the Table 1. The variation of the absorbances peaks revealed a complex degradation process that involves at least the partially oxidation of methylpropyl group and propanoic acid from IBP molecule and as a result mono and di-substituted benzene derivatives are formed. The enhancement of absorbance in the aromatic region suggests this degradation path. The Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂ anodes were more effective in the abatement of absorbance peaks at 196 and 223 nm than Ti/RuO₂-TiO₂ anodes as well as for the absorbance of 240-280 nm region after the absorbance increasing.

Table 1. Absorbance during electrochemical degradation of IBP
c_{ini} = 50 mg/L IBP; pH_{ini} = 11

Anode	Current density/ A/m ²	Electrolysis time/min	Absorbance				
			196 nm	223 nm	258 nm	267 nm	273 nm
Ti/RuO ₂ -TiO ₂	0	0	7.44	2.23	0.06	0.08	0.05
	200	180	6.16	0.73	0.29	0.25	0.18
	300	180	5.43	0.27	0.18	0.16	0.11
Ti/RuO ₂ /SnO ₂ - Sb ₂ O ₅ -RuO ₂	0	0	7.44	2.23	0.06	0.08	0.05
	200	180	6.09	0.36	0.20	0.16	0.11
	300	180	5.05	0.20	0.12	0.10	0.07

The aromatic structure is of about 36.9 % from the molecular weight of IBP. as a result, for absorbance abatement higher than 63.1 % it can be assumed the simultaneous oxidation of substituents and benzenic structure. The best efficiencies for the electrochemical degradation were 87.9 % and 91 % (Table 1), that prove the advanced oxidation of the compound. The above finding is also supported by the TOC values of the electrolysed solutions (Table 2).

Table 2. Working conditions and TOC variation during the IBP degradation on DSA electrodes; c_{ini} = 50 mg/L IBP; pH_{ini} = 11; TOC_{ini} = 51,45 mg C/L

Anode	Current density / A/m ²	Electrolysis time / min	TOC/ mg C/L	TOC abatement /%
Ti/RuO ₂ -TiO ₂	200	180	36.32	29.41
	300	180	34.2	33.53
Ti/RuO ₂ /SnO ₂ - Sb ₂ O ₅ -RuO ₂	200	180	34.77	32.42
	300	180	29.05	43.54

Table 3. Working conditions and CCO-Cr variation during the IBP-CMC degradation on DSA electrodes; c_{ini} = 50 mg/L IBP and 820 mg/L CMC; pH_{ini} = 11; CCO-Cr_{ini} = 655 mg O₂/L

Anode	Current density / A/m ²	Electrolysis time / min	COD/ mg O ₂ /L
Ti/RuO ₂ -TiO ₂	300	180	448
Ti/RuO ₂ /SnO ₂ - Sb ₂ O ₅ -RuO ₂	300	180	466

The experiments were carried out also in solutions containing IPB and CMC. The results (Table 3) revealed that the COD values of electrolysed solutions were less than 500 mgO₂/L, which is the limit for the wastewaters discharge in the sewerage systems according to the Romanian laws.

CONCLUSIONS

The paper dealt with the removal of IBP by electrochemical oxidation on DSA electrodes: Ti/RuO₂-TiO₂ and Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂ in basic medium

The UV spectra and the TOC values of the electrolysed solutions revealed a complex degradation process and the mineralization of IBP during the electrooxidation on both DSA compositions. The best result for TOC abatement was 43.54 % at 300 A/m² and 180 minutes of electrolysis on Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂ anodes.

The experiments were carried out in solutions containing IPB and CMC. The last one can be found in the pharmaceutical effluents because it is an excipient for IBP containing drugs pharmaceutical formulation. The COD values for the electrolysed solutions were of about 450 mg O₂/L for both DSA compositions that would allow the discharge in the sewerage system of a pharmaceutical effluent containing IBP and CMC according to the Romanian laws.

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