

DICLOFENAC DEGRADATION BY PHOTOCATALYTICALLY-ASSISTED ELECTROCHEMICAL METHOD

M. IHOS^{a*}, C. LAZAU^b, F. MANEA^c, L. ANDRES^a, R. PODE^c

^a*National Research and Development Institute for Industrial Ecology–ECOIND, Timisoara Branch, 1 Regina Maria Street, 300 004 Timisoara, Romania
E-mail: monica_ihos@yahoo.com*

^b*Condensed Matter Department, National Institute for Research and Development in Electrochemistry and Condensed Matter, 1 Andronescu Street, 300 254 Timisoara, Romania*

^c*Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University of Timisoara, 6 Parvan Blvd., 300 223 Timisoara, Romania*

Abstract. Diclofenac (DCF), a nonsteroidal anti-inflammatory drug, is a micropollutant resistant to biodegradation. Consequently, it is necessary to apply processes that induce DCF biodegradability or get its mineralisation. The aim of this paper was the investigation of DCF degradation by a photocatalytically-assisted electrochemical method. Dimensionally stable anodes (DSA) consisting of Ti/RuO₂-TiO₂ and zeolite-supported TiO₂ based on (Z-TiO₂-Ag and Z1-TiO₂) photocatalysts were used. The experiments were carried out by applying current densities of 75, 100 and 200 A/m² simultaneously with UV irradiation for 60 and 120 min at concentration of the photocatalysts of 1 g/l. The concentration of DCF in the solutions that underwent degradation increased incrementally: 50, 100 and 200 mg/l. The process was followed by ultraviolet (UV) spectra recording and chemical oxygen demand (COD-Cr) determination. The results showed the effectiveness of this method towards degradation and also mineralisation of DCF. For an initial concentration of 50 mg/l DCF, an applied current density of 200 A/m², 120 min electrolysis and UV irradiation, and Z-TiO₂-Ag photocatalyst, the recorded removal efficiency of COD-Cr was 57.86%.

Keywords: diclofenac, dimensionally stable anodes, photocatalytically-assisted electrochemical degradation.

AIMS AND BACKGROUND

The aim of this study was to assess the degradation of diclofenac (DCF), a nonsteroidal anti-inflammatory drug, by a photocatalytically-assisted electrochemical method. Dimensionally stable anodes (DSA) were used in the electrochemical reactor. The photocatalysts were based on supported TiO₂-zeolite (Z-TiO₂-Ag and Z1-TiO₂). Also, photoelectrochemical experiments were carried out to determinate the contribution of the photocatalysts on pollutant degradation.

* For correspondence.

DCF is one of the most prescribed drugs in the world for pain relief and it can be found in the aquatic environment in the range of ng- μ g/l concentrations^{1,2}, thus it is called a micropollutant. Even at these low concentrations, DCF has undesired effects upon the aquatic organisms^{3,4}.

Wastewaters from pharmaceutical industry are discharged in the sewerage systems and thus pharmaceuticals enter the wastewater treatment plants and pass through them almost unchanged. Therefore, the main source of pharmaceuticals in the aquatic environment is represented by the effluents of wastewater treatment plants^{5,6}.

Electrochemical methods were applied for pollutants detection⁷ or wastewaters treatment⁸ because of their advantages, i.e. versatility and environmental compatibility.

Studies were carried out both for DCF detection^{9,10} and its degradation. Thus, various methods were applied for DCF degradation or removal, as it has been reported: sonoelectrochemical degradation¹¹, adsorption¹²⁻¹⁴, photocatalysis^{15,16} or electrochemical degradation^{17,18}.

The photocatalytically-assisted electrochemical method is very promising with respect to the advanced treatment of pharmaceuticals effluents that contain pharmaceuticals. The anode material is crucial regarding the process evolution and the DSA could be a viable choice because of its electrochemical stability.

EXPERIMENTAL

DCF (2-[2',6'-dichlorophenyl]amino]phenylacetic acid) was supplied by Amoli Organics Ltd as sodium salt and was pharmaceutical grade. Sodium sulphate was purchased from Merck. Distilled water was used for the preparation of the solutions. The working solutions were of 50, 100 and 200 mg/l DCF, respectively, in 0.1 M Na₂SO₄, as supporting electrolyte.

The DSA anodes used were Ti/RuO₂-TiO₂ (molar ratio Ru:Ti in the precursors solution was 30:70) and they were prepared by thermal decomposition of appropriate precursors.

The photocatalysts were based on supported TiO₂-zeolite: Z-TiO₂-Ag (weight ratio in the synthesis mixture zeolite: Ag-modified TiO₂ was 50:1) and Z1-TiO₂ (weight ratio in the synthesis mixture zeolite: TiO₂ was 25:1). The photocatalysts were prepared by hydrothermal method under solid-solid conditions from natural zeolite and Ag-modified TiO₂ or TiO₂. Details regarding the photocatalyst synthesis and characterisation have been published elsewhere¹⁹.

The photocatalytically-assisted electrochemical degradation of DCF was accomplished by using two DSA anodes and three stainless steel cathodes at 1 cm gap. Active surface area was 36 cm². Experiments were carried out by applying current densities of 75, 100 and 200 A/m² at electrolysis time of 60 and 120 min.

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-W, 230 V ~ 50 Hz and 0.32 A. The irradiation was applied on the whole duration of the electrolysis.

The photoelectrochemical experiments were carried out under the same conditions as the photocatalytically-assisted electrochemical ones but in the absence of the photocatalyst.

The samples underwent centrifugation at 5000 rpm and 20 min. A Specord 205 – Analytic Jena spectrophotometer controlled by computer recorded the UV spectra. Also, chemical oxygen demand determination (COD-Cr) was carried out.

RESULTS AND DISCUSSION

The UV spectra of the DCF solutions resulted during the photocatalytically-assisted electrochemical degradation process had the shape as it is shown in Fig. 1, for any concentration of the initial solution, applied current density or time of degradation. The UV spectrum of the DCF in 0.1 M Na₂SO₄ displayed an absorbance peak at 277 nm that flattened during the photocatalytically-assisted electrochemical process, and new maxima appeared in the spectrum.

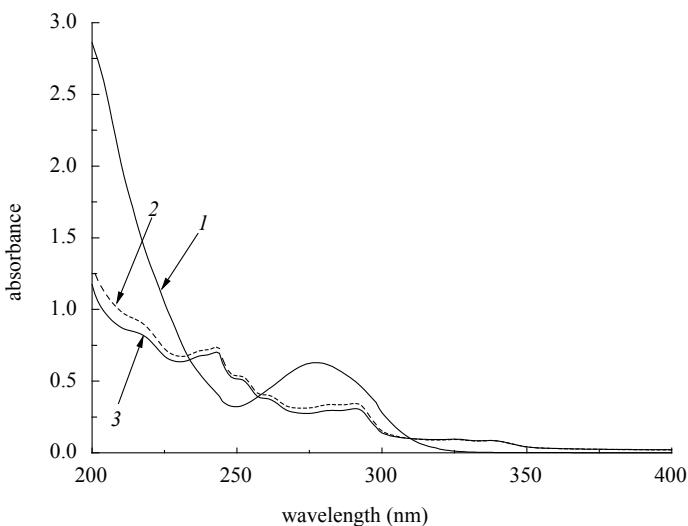


Fig. 1. UV spectra of DCF in 0.1 M Na₂SO₄ Photocatalytically-assisted electrochemical degradation: photocatalyst – Z1-TiO₂; anode – Ti/RuO₂-TiO₂; current density – 100 A/m²; photocatalysis time: 1 – 0 min, 2 – 60 min, 3 – 120 min

This finding anticipated the yielding of DCF degradation products. But, as it is shown in Tables 1–3, the studied process got also the mineralisation of DCF.

The data listed in Table 1 showed for 200 mg/l DCF initial concentration and Z-TiO₂-Ag photocatalysts a directly proportional dependence of the COD-Cr removal efficiency to applied current density at 60 min and inversely proportional at 120 min of photocatalytically-assisted electrochemical process evolution. The best results for COD-Cr removal efficiency were recorded at 75 A/m² both for the photocatalytically-assisted electrochemical and photoelectrochemical process, and the presence of the photocatalyst had not any contribution to DCF mineralisation.

The photocatalytically-assisted electrochemical degradation at DCF initial concentration of 200 mg/l and Z1-TiO₂ photocatalyst revealed a higher COD-Cr removal efficiency at 120 min regardless of applied current density. The inversely proportional dependence of COD-Cr removal efficiency to applied current density was showed for both processes. The data listed in Table 1 showed that for this concentration and working conditions, the presence of the photocatalyst did not get to best results regarding the aromatic ring breakage.

Table 1. Working conditions and COD-Cr evolution in photocatalytically-assisted electrochemical degradation and photoelectrochemical degradation of DCF on Ti/RuO₂-TiO₂ (c_{ini} DCF = 200 mg/l; photocatalysts – Z-TiO₂-Ag and Z1-TiO₂)

Degradation	Current density (A/m ²)	Time (min)	COD-Cr removal efficiency (%)	
			Z-TiO ₂ -Ag	Z1-TiO ₂
Photocatalytically-assisted electrochemical	75	60	47.78	58.66
Photocatalytically-assisted electrochemical	75	120	65.07	63.25
Photoelectrochemical	75	60	75.41	75.41
Photoelectrochemical	75	120	63.25	63.25
Photocatalytically-assisted electrochemical	100	60	50.71	47.41
Photocatalytically-assisted electrochemical	100	120	58.87	59.26
Photoelectrochemical	100	60	63.48	63.48
Photoelectrochemical	100	120	67.91	67.91
Photocatalytically-assisted electrochemical	200	60	53.90	44.07
Photocatalytically-assisted electrochemical	200	120	33.33	49.26
Photoelectrochemical	200	60	50.71	50.71
Photoelectrochemical	200	120	53.90	53.90

The working conditions and COD-Cr evolution for DCF initial concentration of 100 mg/l and the two photocatalysts are presented in Table 2. When Z-TiO₂-Ag photocatalyst was used for both processes: photocatalytically-assisted electrochemical and photoelectrochemical, the COD-Cr removal efficiency was higher at 75 A/m² and 120 min. Also, COD-Cr removal efficiency was higher for the photoelectrochemical process, consequently the contribution of the photocatalyst was not significant in the photocatalytically-assisted electrochemical process.

The examination of the data listed in Table 2 for Z1-TiO₂ photocatalyst showed that the photocatalytically-assisted electrochemical degradation was more efficient at 120 min regardless of the applied current density. The best results for COD-Cr removal efficiency were recorded at the lower of applied current density, namely 75 A/m², both in the presence and absence of the photocatalyst. The presence of the photocatalyst got to better results regarding COD-Cr removal efficiency only for 75 A/m² and 120 min.

Table 2. Working conditions and COD-Cr evolution in photocatalytically-assisted electrochemical degradation and photoelectrochemical degradation of DCF on Ti/RuO₂-TiO₂ (c_{ini} DCF = 100 mg/l; photocatalysts – Z-TiO₂-Ag and Z1-TiO₂)

Degradation	Current density (A/m ²)	Time (min)	COD-Cr removal efficiency (%)	
			Z-TiO ₂ -Ag	Z1-TiO ₂
Photocatalytically-assisted electrochemical	75	60	42.07	62.96
Photocatalytically-assisted electrochemical	75	120	49.62	73.26
Photoelectrochemical	75	60	65.10	65.10
Photoelectrochemical	75	120	66.59	66.59
Photocatalytically-assisted electrochemical	100	60	26.67	29.22
Photocatalytically-assisted electrochemical	100	120	49.82	35.32
Photoelectrochemical	100	60	41.17	41.17
Photoelectrochemical	100	120	52.92	52.92
Photocatalytically-assisted electrochemical	200	60	–	32.47
Photocatalytically-assisted electrochemical	200	120	–	35.32
Photoelectrochemical	200	60	–	41.17
Photoelectrochemical	200	120	–	44.16

New findings were made when the data shown in Table 3 were taken into consideration. When the pollutant concentration was 50 mg/l in the presence of Z-TiO₂-Ag photocatalyst, the COD-Cr removal efficiency was higher than that during the photoelectrochemical process. The best results were recorded at 120 min for both applied current densities.

The same behaviour was observed for DCF concentration of 50 mg/l and Z1-TiO₂ photocatalyst. Both processes took place with higher efficiency at 120 min, and the presence of the photocatalyst got to higher COD-Cr removal efficiency than the photoelectrochemical process. The best results were recorded for the photocatalytically-assisted electrochemical degradation at 200 A/m².

Table 3. Working conditions and COD-Cr evolution in photocatalytically-assisted electrochemical degradation and photoelectrochemical degradation of DCF on Ti/RuO₂-TiO₂ (*c*_{ini} DCF =50 mg/l; photocatalysts – Z-TiO₂-Ag and Z1-TiO₂)

Degradation	Current density (A/m ²)	Time (min)	COD-Cr removal efficiency (%)	
			Z-TiO ₂ -Ag	Z1-TiO ₂
Photocatalytically-assisted electrochemical	75	60	–	25.52
Photocatalytically-assisted electrochemical	75	120	–	50.00
Photoelectrochemical	75	60	–	19.05
Photoelectrochemical	75	120	–	42.84
Photocatalytically-assisted electrochemical	100	60	52.11	23.76
Photocatalytically-assisted electrochemical	100	120	57.86	26.74
Photoelectrochemical	100	60	14.30	14.30
Photoelectrochemical	100	120	19.03	19.03
Photocatalytically-assisted electrochemical	200	60	47.30	41.65
Photocatalytically-assisted electrochemical	200	120	57.86	52.31
Photoelectrochemical	200	60	12.50	12.50
Photoelectrochemical	200	120	22.21	22.21

CONCLUSIONS

This study was focused on photocatalytically-assisted electrochemical degradation of DCF, a biorefractory pollutant, by using DSA anodes and photocatalysts based on supported TiO₂-zeolite. Photoelectrochemical experiments were carried out to find out the contribution of the photocatalyst to the degradation and mineralisation of the pollutant.

The results revealed that the photocatalytically-assisted electrochemical degradation by using Ti/RuO₂-TiO₂ anode both in the presence of Z-TiO₂-Ag and Z1-TiO₂ photocatalysts got higher COD-Cr removal efficiency than photoelectrochemical degradation only for DCF concentration of 50 mg/l regardless of the applied current density.

The contribution of the Z-TiO₂-Ag photocatalysts to COD-Cr removal efficiency was 35.65% at 120 min of electrolysis and UV irradiation, and an applied current density of 200 A/m². Under the same working conditions, the contribution of Z1-TiO₂ photocatalyst was 30.10%.

Acknowledgements. This work was supported by a grant of the Romanian National Authority for Scientific Research – Core Program 13N/2009, Environmental Research – priority in sustainable industrial development – MEDIND, Project code PN 09 -13 03 02.

REFERENCES

1. J.-Q. JIANG, Z. ZHOU, S. PATIBANDLA, X. SHU: Pharmaceutical Removal from Wastewater by Ferrate (Vi) and Preliminary Effluent Toxicity Assessment by Zebrafish Embryo Model. *Microchem J*, **110**, 239 (2013).
2. K. KUMMERER: The Presence of Pharmaceuticals in the Environment due to Human Use – Present Knowledge and Future Challenges. *J Environ Manage*, **90** (8), 2354 (2009).
3. L. H. M. L. M. SANTOS, A. N. ARAUJO, A. FACHINI, A. PENA, C. DELERUE-MATOS, M. C. B. S. M. MONTENEGRO: Ecological Aspects Related to the Presence of Pharmaceuticals in the Aquatic Environment. *J Hazard Mater*, **175**, 45 (2010).
4. R. TRIEBSKORN, H. CASPER, A. HEYD, R. EIKEMPER, H.-R. KOHLER, J. SCHWAIGER: Toxic Effects of the Non-steroidal Antiinflammatory Drug Diclofenac. Part II. Cytological Effects in Liver, Kidney, Gills and Intestine of Rainbow Trout (*Oncorhynchus mykiss*). *Aquat Toxicol*, **68** (2), 151 (2004).
5. B. PETRIE, R. BARDEN, B. KASPRZYK-HORDEN: A Review on Emerging Contaminants in Wastewaters and the Environment: Current Knowledge, Understudied Areas and Recommendations for Future Monitoring. *Water Res*, **72**, 3 (2015).
6. M. GROS, M. PETROVIC, A. GINEBREDA, D. BARCELO: Removal of Pharmaceuticals during Wastewater Treatment and Environmental Risk Assessment Using Hazard Indexes. *Environ Int*, **36**, 15 (2010).
7. J. SAVIC, V. VASIC, C. CRISTEA, R. SANDULESCU: Electrochemical Behaviour of Bis-pyrazole-azochromotropic Acid and Its Use as Modifier for Elaboration of Potentiometric Sensor for the Copper Detection. *J Environ Prot Ecol*, **10** (4), 1162 (2009).
8. B. MALINOVIC, M. G. PAVLOVIC, S. BUNIC: Treatment of Copper Cyanide Wastewaters in Treatment of Copper Cyanide Wastewaters in Electrochemical Batch Reactor with Stainless Steel Electrodes Electrochemical Batch Reactor with Stainless Steel Electrodes. *J Environ Prot Ecol*, **15** (4), 1574 (2014).
9. F. MANEA, M. IHOS, A. REMES, G. BURTICA, J. SCHOONMAN: Electrochemical Determination of Diclofenac Sodium in Aqueous Solution on Cu-doped Zeolite-expanded Graphite-Epoxy Electrode. *Electroanal*, **22** (17–18), 2058 (2010).
10. M. IHOS, A. REMES, F. MANEA: Electrochemical Determination of Diclofenac in Water Using Boron-doped Diamond Electrode. *J Environ Prot Ecol*, **13** (4), 2096 (2012).
11. P. FINKBEINER, M. FRANKE, F. ANSCHUETZ, A. IGNASZAK, M. STELTER, P. BRAEUTIGAM: Sonoelectrochemical Degradation of the Anti-inflammatory Drug Diclofenac in Water. *Chem Eng J*, **273**, 214 (2015).
12. H. WEI, S. DENG, Q. HUANG, Y. NIE, B. WANG, J. HUANG, G. YU: Regenerable Granular Carbon Nanotubes/Alumina Hybrid Adsorbents for Diclofenac Sodium and Carbamazepine Removal from Aqueous Solution. *Water Res*, **47**(12), 4139 (2013).
13. C. SAUCIER, M. A. ADEBAYO, E. C. LIMA, R. CATALUNA, P. S. THUE, L. D.T. PROLA, M. J. PUCHANA-ROSETO, F. M. MACHADO, F. A. PAVAN, G. L. DOTTO: Microwave-assisted Activated Carbon from Cocoa Shell as Adsorbent for Removal of Sodium Diclofenac and Nimesulide from Aqueous Effluents. *J Hazard Mater*, **289**, 18, (2015).
14. J. L. SOTELO, A. RODRIGUEZ, S. ALVAREZ, J. GARCIA: Removal of Caffeine and Diclofenac on Activated Carbon in Fixed Bed Column. *Chem Eng Res Des*, **90** (7), 967 (2012).
15. L. RIZZO, S. MERIC, D. KASSINOS, M. GUIDA, F. RUSSO, V. BELGIORNO: Degradation of Diclofenac by TiO₂ Photocatalysis: UV Absorbance Kinetics and Process Evaluation through a Set of Toxicity Bioassays. *Water Res*, **43** (4), 979 (2009).

16. C. MARTINEZ, M. CANLE, M. I. FERNANDEZ, J. A. SANTABALLA, J. FARIA: Aqueous Degradation of Diclofenac by Heterogeneous Photocatalysis Using Nanostructured Materials. *Appl Catal B-Environ.*, **107** (1–2), 110 (2011).
17. E. BRILLAS, S. GARCIA-SEGURA, M. SKOUMAL, C. ARIAS: Electrochemical Incineration of Diclofenac in Neutral Aqueous Medium by Anodic Oxidation Using Pt and Boron-doped Diamond Anodes. *Chemosphere*, **79** (6), 605 (2010).
18. X. ZHAO, Y. HOU, H. LIU, Z. QIANG, J. QU: Electro-oxidation of Diclofenac at Boron-doped Diamond: Kinetics and Mechanism. *Electrochim Acta*, **54**, 4172 (2009).
19. C. LAZAU, C. RATIU, C. ORHA, R. PODE, F. MANEA: Photocatalytic Activity of Undoped and Ag-doped TiO₂-supported Zeolite for Humic Acid Degradation and Mineralization. *Mater Res Bull*, **46** (11), 1916 (2011).

Received 19 October 2015

Revised 25 November 2015