

Pharmaceutically Active Compounds Degradation Using Doped TiO₂ Functionalized Zeolite Photocatalyst

MONICA IHOS^{1*}, CORNELIU BOGATU², CARMEN LAZAU³, FLORICA MANEA⁴, RODICA PODE⁴

¹National Research and Development Institute for Industrial Ecology ECOIND, Timisoara Subsidiary, 115 Bujorilor Str., 300431, Timisoara, Romania

²Independent Researcher, Timisoara, 9 Soroca Str., 300666 Timisoara, Romania

³National Institute for Research and Development in Electrochemistry and Condensed Matter, 1 Plautius Andronescu Str., 300254, Timisoara, Romania

⁴“Politehnica” University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Vasile Parvan Blvd., 300223, Timisoara, Romania

The aim of this study was the investigation of photocatalytic degradation of pharmaceutically active compounds using doped TiO₂ functionalized zeolite photocatalyst. Diclofenac (DCF), a non-steroidal anti-inflammatory drug, that represents a biorefractory micropollutant, was chosen as model of pharmaceutically active compound. The photocatalyst was Z-TiO₂-Ag. The concentration of DCF in the working solutions was 10 mg/L, 50 mg/L, 100 mg/L and 200 mg/L and of photocatalyst 1 g/L in any experiments. The process was monitored by recording the UV spectra of the treated solutions and total organic carbon (TOC) determination. The UV spectra analysis and TOC removal proved that along the advanced degradation of DCF also a mineralization process occurred. The carried out research provided useful information envisaging the treatment of pharmaceutical effluents by photocatalysis.

Keywords: diclofenac, pharmaceutically active compounds, photocatalytic degradation

The presence of biorefractory pollutants in waters has raised concerns worldwide because they are harmful to the environment. The biorefractory pollutants pass unchanged through the wastewater treatment plants (WWTPs) and thus they enter the water bodies. Photocatalysis is one of the Advanced Oxidation Processes (AOPs) suitable for biorefractory pollutants degradation and mineralization. Thus, were degraded p-toluenesulfonic acid, methylene blue dye, nicotine, 4-iso propyl phenol, diazinon, indigo carmine dye, phenol, sulfaclozine, acid blue 74 dye, 5-fluorouracil, rhodamine 6G, triclosan, 4-chloroaniline, 2,4,6-trinitrotoluene using photocatalyst as P-25 TiO₂, Pd/TiO₂ nanocomposite, commercial ZnO/TiO₂, ZnO-TiO₂ composite, TiO₂ quantum dots, Ag core- TiO₂ shell or Ag-Ag₂O-ZnO nanostructures anchored on graphene oxide, P-25 TiO₂ impregnated with 2% WO₃, ZnO and Mn-doped ZnO nanoparticles, Fe-TiO₂ and Ni-doped TiO₂ sol-gel nanopowders under solar, visible, ultraviolet radiation or UV-Vis light [1-16].

To enhance the available surface area of immobilized TiO₂ and to obtain a stable, efficient and economical photocatalyst, various catalyst supports has been used for photocatalytic degradation of pharmaceuticals that represents a new class of emerging pollutants: sand, activated carbon or side-glowing optical fibers [17-19]. Also, an inert and ideal support for the photocatalyst is the zeolite that is an eco-friendly material and good adsorbent due to its high surface area and high thermal stability [20].

The aim of this study was the degradation of diclofenac (DCF), a non-steroidal anti-inflammatory drug, using doped TiO₂ functionalized zeolite as photocatalyst, to provide helpful information for application of photocatalysis to pharmaceutical effluents treatment.

Experimental part

Photocatalytic degradation of DCF

DCF, {2-[(2,6-Dichlorophenyl)amino]phenyl}acetic acid, was supplied by Amoli Organics Ltd as sodium salt and

was pharmaceutical grade. The photocatalyst, Z-TiO₂-Ag (weight ratio in the synthesis mixture zeolite: Ag-modified TiO₂ 50:1), was prepared by hydrothermal method under solid-solid conditions from natural zeolite from Mirsid, Romania and Ag-modified TiO₂. Details regarding the photocatalyst synthesis and characterization have been previously reported [21].

Distilled water was used for the solutions preparation. The experiments were carried out using 200 ml solutions of 10 mg/L, 50 mg/L, 100 mg/L and 200 mg/L DCF. The concentration of photocatalyst was of 1 g/L in any experiments and it was 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 Amps. The samples taken periodically underwent centrifugation 15 min at 5000 rpm.

Analytical methods

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

Results and discussions

Photocatalytic degradation of DCF

The chemical structure and the UV spectrum of DCF are shown in figures 1 and 2, respectively. The UV spectrum exhibits two absorption bands with maxima at 201 nm and 277 nm.

The UV spectra related to the photocatalytic degradation of solution of 10 mg/L DCF mediated by Z-TiO₂-Ag, for reaction time in the range of 5-540 min, are shown in figures

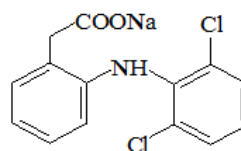


Fig. 1. Chemical structure of DCF

* email: monica_ihos@yahoo.com; Phone.: 0040 356 008221

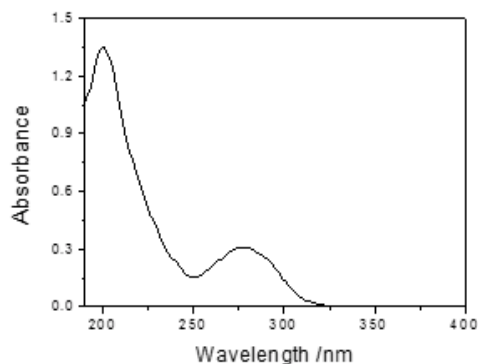


Fig. 2. UV spectrum of DCF

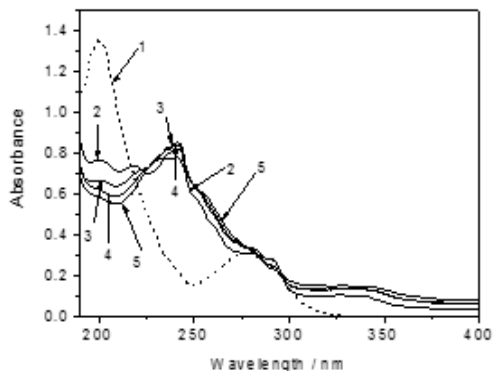


Fig. 3. UV spectra of DCF photocatalyst: Z-TiO₂-Ag; DCF concentration: 10 mg/L; photocatalysis time: 1- 0 min; 2- 5 min; 3- 10 min; 4- 15 min; 5- 60 min

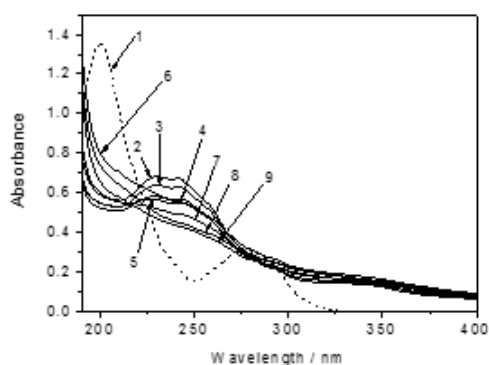


Fig. 4. UV spectra of DCF photocatalyst: Z-TiO₂-Ag; DCF concentration: 10 mg/L; photocatalysis time: 1- 0 min; 2- 120 min; 3- 180 min; 4- 240 min; 5- 300 min; 6- 360 min; 7- 420 min; 8- 480 min; 9- 540 min

3 and 4. The UV spectra analysis versus time was carried out by analysing the absorption bands characteristic for the aromatic compounds: ethylenic band in the range of 180-220 nm (E), conjugated band in the range of 220-250 nm (K), benzenoid band in the range of 250-290 nm (B) and radical-like band in the range of 275-330 nm (R) [22].

The initial spectrum of DCF, with absorption maxima at 201 and 277 nm, showed changes after 5 min of photocatalysis. The maximum at 201 nm that belongs to ethylenic band diminished by 43.7% and the new absorption bands exhibited maxima at 218, 241, 282 and 327 nm in the first minutes. The appearance of ethylenic band at 218 nm indicated the partially split of the two aromatic rings and it can be assigned to sodium salt of (2-Aminophenyl)acetic acid. The prominent absorption maximum at 241 nm is characteristic for aromatic conjugated systems, with unsaturated functional groups and it can be also assigned to (2-Aminophenyl)acetic acid [23].

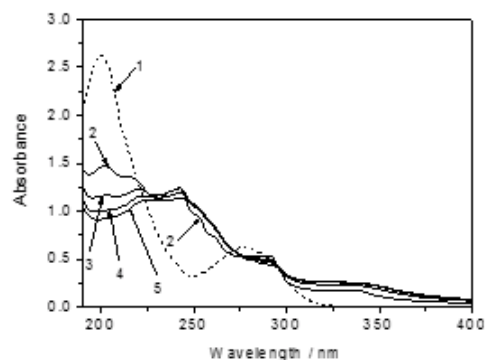


Fig. 5. UV spectra of DCF photocatalyst: Z-TiO₂-Ag; DCF concentration: 50 mg/L; photocatalysis time: 1- 0 min; 2- 15 min; 3- 30 min; 4- 45 min; 5- 60 min

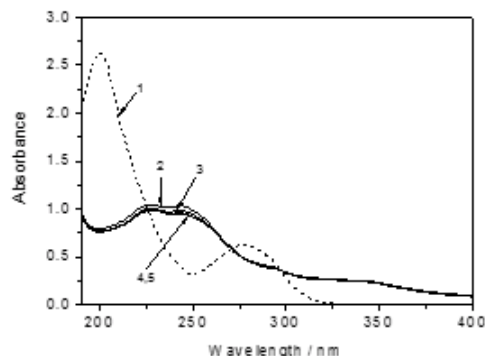


Fig. 6. UV spectra of DCF photocatalyst: Z-TiO₂-Ag; DCF concentration: 50 mg/L; photocatalysis time: 1- 0 min; 2- 120 min; 3- 180 min; 4- 240 min; 5- 300 min

The contribution in spectrum of DCF, (2-Aminophenyl)acetic acid and 1,3-Dichlorobenzene is highlighted by the benzenoid band with maximum at 282 nm, more intense for the higher concentrations of 50 mg/L, 100 mg/L and 200 mg/L DCF (figs. 5-10).

The radical-like band with maximum at 327 nm revealed the presence of an aromatic compound with groups that have non-participating electrons, as it is the sodium salt of (2-Aminophenyl)acetic acid.

After the first 5 min the process was slow. Thus, after 240 min of photocatalysis the maximum of absorbance at 201 nm decreased with 60.7% compared to the initial one of the DCF; also, the intensity of the peak at 218 nm decreased by 22.8%. The partial conversion (2-Aminophenyl) acetic acid versus time was suggested by the abatement conjugated band absorption at 241 nm and 240 min of photocatalysis by 30.5% as opposed to that at 5 min at and it represented the second step of the process.

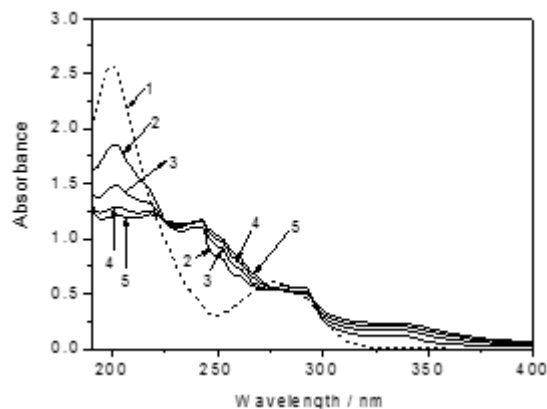


Fig. 7. UV spectra of DCF photocatalyst: Z-TiO₂-Ag; DCF concentration: 100 mg/L; photocatalysis time: 1- 0 min; 2- 15 min; 3- 30 min; 4- 45 min; 5- 60 min

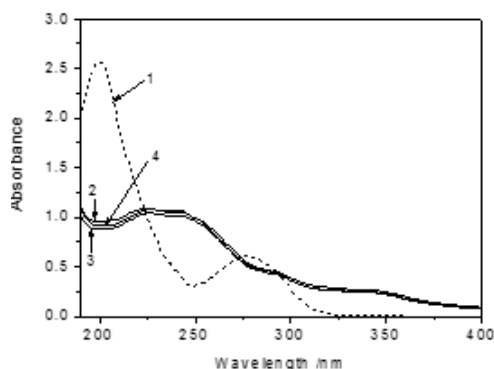


Fig. 8. UV spectra of DCF photocatalyst: Z-TiO₂-Ag; DCF concentration: 100 mg/L; photocatalysis time: 1- 0 min; 2- 120 min; 3- 180 min; 4- 240 min

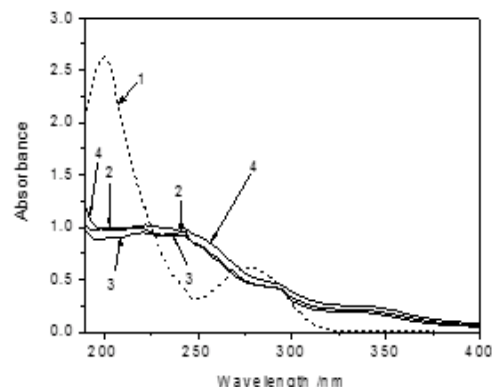


Fig. 10. UV spectra of DCF photocatalyst: Z-TiO₂-Ag; DCF concentration: 100 mg/L; photocatalysis time: 1- 0 min; 2- 120 min; 3- 180 min; 4- 240 min

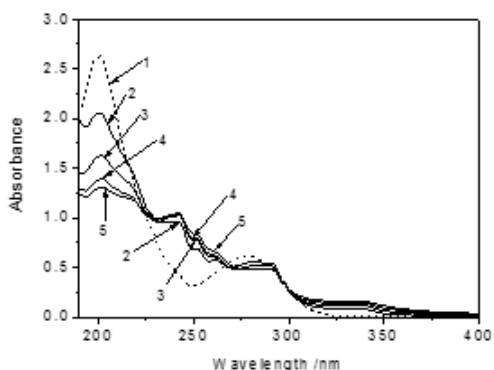


Fig. 9. UV spectra of DCF photocatalyst: Z-TiO₂-Ag; DCF concentration: 200 mg/L; photocatalysis time: 1- 0 min; 2- 15 min; 3- 30 min; 4- 45 min; 5- 60 min

After 360 min of photocatalysis, the spectrum in the ethylenic and conjugated regions changed its shape into a descending curve that corresponded to the third step of oxidation, that of benzene rings one (fig. 4).

For the concentration of 50 mg/L DCF, the ethylenic band abatement, 44.1% in the first 15 min of photocatalysis, was close to that determined for 10 mg/L DCF (fig. 5). At higher concentrations the descending variation was of 29.1% for 100 mg/L DCF and 21.5% for 200 mg/L DCF (figs. 7 and 9).

In the second step for the concentration of 50 mg/L DCF and 300 min of photocatalysis, the conjugated band

presented a lower intensity by 22.7% compared to the one determined after 15 min. For the higher concentration, of 100 and 200 mg/L DCF, the abatement was of 7.3% and 3.2%, respectively after 180 min of photocatalysis.

Data regarding the absorbance abatement at 201, 241 and 282 nm, after various photocatalysis time is listed in table 1. The maximum absorbance determined for the DCF concentrations at 327 nm were of 0.19 (420 min), 0.28 (420 min), 0.29 (300 min) and 0.30 (300 min), respectively. These values for the absorbance of radical-like band, corresponding to (2-Aminophenyl)acetic acid, showed the limitation of photocatalytic oxidation in the presence of Z-TiO₂-Ag photocatalyst, in the applied working conditions: the splitting of the two rings of DCF and their partial oxidation reached a maximum for 50 mg/L DCF and for higher concentrations the value of absorbance was kept practically constant.

The above data revealed that the process occurred to a more advanced extent, in three steps for 10 mg/L DCF. For higher concentrations only the first two steps occurred.

DCF Mineralization

The TOC removal was listed in table 2 and the results revealed that a mineralization process occurred along with DCF photocatalytic degradation. The TOC removal ranged from about 28 to about 53% and the best results were recorded for 50 mg/L DCF.

Table 1

ABATEMENT OF DCF ABSORPTION VERSUS THE TIME OF PHOTOCATALYTIC OXIDATION MEDIATED BY Z-TiO₂-Ag FOR ETHYLENIC, CONJUGATED AND BENZENOID BANDS

DCF concentration / mg/L	Time / min	Absorption abatement / %		
		201 nm	241 nm	282 nm
10	420	57.0	40.2	10.0
50	420	70.1	22.8	21.6
100	300	65.1	0.90	13.3
200	300	64.4	-	6.7

DCF concentration / mg/L	Time / min	TOC removal / %
50	240	42.9
	300	52.7
100	240	28.4
	300	32.0
200	240	35.0
	300	36.1

Table 2
WORKING CONDITIONS AND TOC REMOVAL AT VARIOUS DCF CONCENTRATIONS FOR THE PHOTOCATALYTIC OXIDATION MEDIATED BY Z-TiO₂-Ag

Conclusions

This study dealt with the photocatalytic degradation of DCF mediated by silver doped TiO₂ functionalized zeolite.

The UV spectra analysis showed that the process occurred following three steps: (i) the partially split of aromatic rings of DCF, (ii) the partially conversion of degradation products yielded in the first step and (iii) oxidation of benzene rings.

The photodegradation process took place to a larger extent for the lowest concentration, namely 10 mg/L DCF.

TOC removal revealed that along with the photodegradation a mineralization process of DCF occurred. Among the concentration of 50, 100 and 200 mg/L, respectively, at 300 min of photocatalysis, the first one exhibited the best value for TOC removal, of 52.7%.

Acknowledgements: This work was supported by a grant of the Ministry of Research and Innovation – Program Nucleu, contract no. 13N/2009, Environmental Research – Priority in Sustainable Industrial Development – MEDIND, Project code PN 09 -13 03 02.

References

1. AMRUTA, S., VIDYA, S.K., Sol. Energy, **127**, 2016, p. 67.
2. ESPINA DE FRANCO, M.A., DA SILVA, W.L., BAGNARA, M., AZARIO LANSARIN, M., DOS SANTOS, J.H.Z., Sci. Total Environ., **494–495**, 2014, p. 97
3. CONSTANTIN, L.A., NITOI, I., CRISTEA, I., OANCEA, P., Rev. Chim. (Bucharest), **67**, no. 8, 2016, p. 1447
4. KAMBLE, S., P., SAWANT, S., B., PANGARKAR, V., G., J. Hazard. Mater., **140**, 2007, p. 149
5. ABDELAAL, M.Y., MOHAMED, R.M., J. Alloy. Compd., **576**, 2013, p. 201
6. SOOD S., KUMAR, S., UMAR, A., KAUR, A., MEHTA, K. S., KANSAL, S. K., J. ALLOY. COMPD., **650**, 2015, p. 193
7. NITOI, I., OANCEA, P., CONSTANTIN, L.A., CRISAN, M., CRISAN, D., CRISTEA, I., CONSTANTIN, M.A., International Symposium The Environment and the Industry, 2016, p. 285
8. ISMAIL, L., RIFAI, A., FERRONATO, C., FINE, L., JABER, F., CHOVELON, J.- M., Appl. Catal. B-Environ., **185**, 2016, p. 88
9. LUTIC, D., CRETESCU, I., Rev. Chim. (Bucharest), **67**, no. 1, 2016, p. 134
10. UMUKORO, E.H., PELEYEJU, M.G., NGILA, J.C., AROTIBA, O.A., Solid State Sci., **51**, 2016, p. 66
11. NITOI, I., OANCEA, P., CRISTEA, I., International Symposium The Environment and the Industry, **1**, 2013, p. 108
12. JONIDI-JAFARI, A., SHIRZAD-SIBONI, M., YANG, J.-K., NAIMI-JOUBANI, M., FARROKHI, M., J. Taiwan Inst. Chem. Eng., **50**, 2015, p. 100
13. CONSTANTIN, L., NITOI, I., CRISTEA, I., OANCEA, P., ORBECI, C., NECHIFOR, A.C., Rev. Chim. (Bucharest), **66**, no. 5, 2015, p. 597
14. YASMINA, M., MOURAD, K., MOHAMMED, S.H., KHAOULA, C., Energy Procedia, **50**, 2014, p. 559
15. (BUSILA) IBANESCU, M., MUSAT, V., TEXTOR, T., MAHLTIG, B., Rev. Chim. (Bucharest), **65**, no. 6, 2014, p. 689.
16. RAILEANU, M., CRISAN, M., IANCULESCU, A., CRISAN, D., DRAGAN, N., OSICEANU, P., SOMACESCU, S., STANICA, N., TODAN, L., NITOI, I., Water Air. Soil Pollut., **224**, 2013, p. 1
17. HE, Y., SUTTON, N.B., RIJNAARTS, H.H.H., LANGENHOFF, A.A.M., Appl. Catal. B-Environ., **182**, 2016, p. 132
18. LIN, L., WANG, H., XU, P., Chem. Eng. J., **310**, 2017, p. 389
19. ALALM, M.G., TAWFIK, A., OOKAWARA, S., J. Environ. Chem. Eng., **4**, 2016, p. 1929
20. YU, H., CUI, T., LIU, Z., J. Energy. Chem., **25**, 2016, p. 621
21. LAZAU, C., RATIU, C., ORHA, C., PODE, R., MANEA, F., Mater. Res. Bull., **46**, no. 11, 2011, p. 1916
22. ISAC-GARCIA, J., DOBADO, J.A., CALVO-FLORES, F.G., MARTINEZ-GARCIA, H., Experimental Organic Chemistry: Laboratory Manual, 1st Edition, Academic Press - Elsevier, London-San Diego-Waltham-Oxford, 2015, p. 156
23. BRENNAN, N.F., PhD Thesis Structural studies of thallium(I)-thiourea complexes, University of Pretoria etd-Brennan, NF, 2006, p. 109

Manuscript received: 11.11.2017