

ANALYTICAL CONTROL OF DICLOFENAC REMOVAL IN THE PHOTOCATALYTIC OXIDATION PROCESS

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Continuously increasing pharmaceuticals consumption contributes to the increase of their concentration in the aqueous environment, which is at a level of a few ng/dm^3 to several $\mu\text{g}/\text{dm}^3$. A numerous group of pharmaceuticals occurring in surface waters are non-steroidal painkillers and anti-inflammatory drugs, which include diclofenac. The paper presents the possibility of the analytical control of diclofenac photocatalytic oxidation process in the aquatic environment. To examine the effectiveness of the process various instrumental methods including HPLC analysis preceded with solid phase extraction SPE, measurements of UV absorbance and total organic carbon were used.

Keywords: diclofenac, photocatalysis, SPE, HPLC, absorbance in UV, total organic carbon

1. INTRODUCTION

Micropollutants of pharmaceutical activity (drugs and their metabolites), apart from hormones and other endocrine substances i.e. perfluorinated acids both carboxylic and sulphonate, substances acting only as UV filters, naphthenic acids, dioxines, benzotriazoles, additives for liquid fuels, bromated derivatives of aromatic compounds and by-products of disinfection are included to the group of the antropogenic organic micropollutants [8,11].

Particular attention should be paid to the group of medicines which are available without prescription and the most commonly appear in water environment. This group includes non-steroidal painkillers and anti-inflammatory drugs which can be represented by diclophenac [1,13].

The concentration of pharmaceuticals and their metabolites in water environment is of a few ng/dm^3 to several $\mu\text{g}/\text{dm}^3$ and depends on the load of

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pharmaceutical contaminants in the treated wastewater, which is deposited to natural water reservoirs. The vast majority of research on the concentration of pharmaceuticals in water environment [2,5] shows that their low concentration have insignificant influence on water organisms subjected to short-term exposure of each pharmaceutical. However, it is not known what are the effects of the long-term exposure to seemingly low concentration of substances recognized as highly biologically reactive. Since there is no particular data concerning the toxic effect of pharmaceuticals present in water environment on living organisms including humans, it is necessary to eliminate them completely from water intended for human consumption.

The total removal of pharmaceuticals from wastewater or surface water (a potential source of drinking water) is a difficult procedure considering their polar structure as well as slight susceptibility to biochemical decomposition [6,10,12]. Photocatalytic oxidation is an alternative to the commonly used sorption and coagulation processes for surface water treatment or activated sludge microorganisms for wastewater treatment [3,4,7,9]. The evaluation of the effectiveness of photocatalysis and the selection of process parameters, which include, the choice of photocatalyst, pH, duration of the process and the wavelength is possible basing on the knowledge of the test compounds concentration in aquatic environment. The study on oxidation processes enables the determination of the possibility and the rate of the removed compound decomposition. Nevertheless, the resulting oxidation byproducts can reduce the final treatment effect. Thus, only a reduction of the initial compound concentration is observed, oppositely its degradation pathway.

The paper presents the possibility of analytical control of diclofenac removal from aquatic environment in the photocatalytic oxidation process. Various instrumental methods including HPLC analysis preceded with solid phase extraction SPE, UV absorbance and total organic carbon measurements were used to examine the effectiveness of the process.

2. EXPERIMENTAL

2.1. Apparatus, materials, reagents

Diclofenac in the form of diclofenac sodium salt supplied by Sigma-Aldrich (Poland) was used as a pattern of non-steroidal painkiller and anti-inflammatory drug.

Titanium dioxide (TiO₂) by Evonik Degussa (Germany) marked with the symbol P25 was used as catalyst.

Methanol, acetonitrile and water for HPLC were supplied by POCH S.A.

SPE Supelclean™ ENVI-8 tubes of a volume of 6 cm³ (1.0 g) by Supelco and a SPE chamber also by Supelco were used during the solid phase extraction.

Heraeus laboratory reactor equipped with an immersed medium pressure lamp of 150 W.

Aeration pump with a capacity of 0.25 cm³ air for 1 h.

Filtration set connected to a vacuum pump from AGA Labor equipped with glass fiber filters (0.45 μm) by Millipore.

2.2. Test samples

In the study, the simulated solutions were prepared on deionized water matrix, to which diclofenac in a constant concentration of 1 mg/dm³ was introduced. The high concentration of the drug i.e. much higher than the environmental one, was used in order to increase the precision of the performed analytical measurements.

The solution pH was adjusted to 7 using 0.1 mol/dm³ HCl and 0.1 mol/dm³ NaOH.

The water solutions after addition of the catalyst (TiO₂) were undergone the photocatalytic oxidation process at different times i.e. 5, 15, 30, and 60 min.

2.3. Diclofenac determination procedure

The determination of diclofenac in the solutions before and after the photocatalytic oxidation process was preceded by the catalyst particles separation with the use of a glass fibers filter. Next,

- quantitative analysis of the tested drug with high performance liquid chromatography HPLC preceded by solid phase extraction SPE,
- measurement of UV absorbance,
- measurement of total organic carbon (TOC),
- measurement of conductivity

were performed.

The determination of diclofenac concentration was made using solid phase extraction SPE and HPLC analysis. The octylsilan tube phase (C8) was firstly conditioned with 5cm³ of methanol and next washed with 5 cm³ of distilled water of pH 7. Water sample of a volume 20 cm³ (pH = 7) was used in the procedure. After the extraction the colum bed was dried for 5 min at vacuum. The separated compound was washed out with 1 cm³ of methanol and dried in a nitrogen stream. After dissolution of the sample in 100 cm³ of methanol it was subjected to HPLC analysis. A high performance liquid chromatograph Varian HPLC (UV detector, wavelength $\lambda = 220$ nm) was used. It was equipped with Hypersil GOLD column by Thermo Scientific of length 25 cm, diameter 4.6 mm and granulation – 5μm. The mobile phase consisted of a mixed water and acetonitrile in the ratio of 85:15 (v/v).

In the preliminary work the diclofenac maximum absorbance ($\lambda_{\max} = 276$ nm) was identified from a designated UV-VIS spectra registered using of the

UV-VIS spectrophotometer Cecil 1000 by Jena AG for the wavelength range from 200 to 400 nm (Fig. 1).

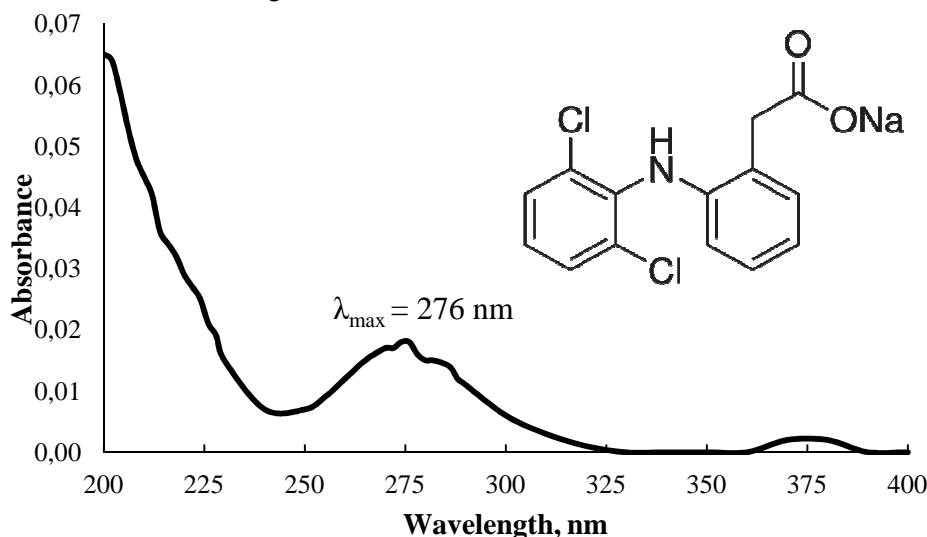


Fig. 1. UV-VIS spectrum of diclofenac sodium salt and its chemical structure

The measurement of total organic carbon was performed using multi C/N analyzer to liquid and solid samples IDC Analytik Jena by Jena AG.

3. RESULTS AND DISCUSSION

The decrease of diclofenac concentration during the photocatalysis process was determined by the use of HPLC analysis, which was preceded by solid phase extraction SPE (Fig. 2). The analyte separation efficiency and its precision (expressed by the average standard deviation,%) were determined basing on results obtained for four extractions. It was found that the extraction yield of diclofenac was 60% and the precision of determination between individual samples did not exceed 0.65%.

The chromatographic determination conducted for water sampled during the photocatalytic oxidation showed the decrease of the diclofenac concentration. It revealed that the removal efficiency increased with the elongation of the oxidation process (Fig. 2). The oxidation of the investigated compound carried out without the addition of catalyst (photolysis) was made as a comparative treatment. The obtained results confirmed that the presence of catalyst favored the pharmaceutical oxidation and after a 30 minute exposure 90% reduction of the pharmaceutical concentration was observed.

The elongation of the exposure time did not result in the increase of the value of the parameter. Additional peaks at the chromatogram were not

observed, thus it was supposed that the formation of by-products during the oxidation of diclofenac did not occur. However, in order to confirm this observation GC-MS analysis, which is a more accurate method, should be performed.

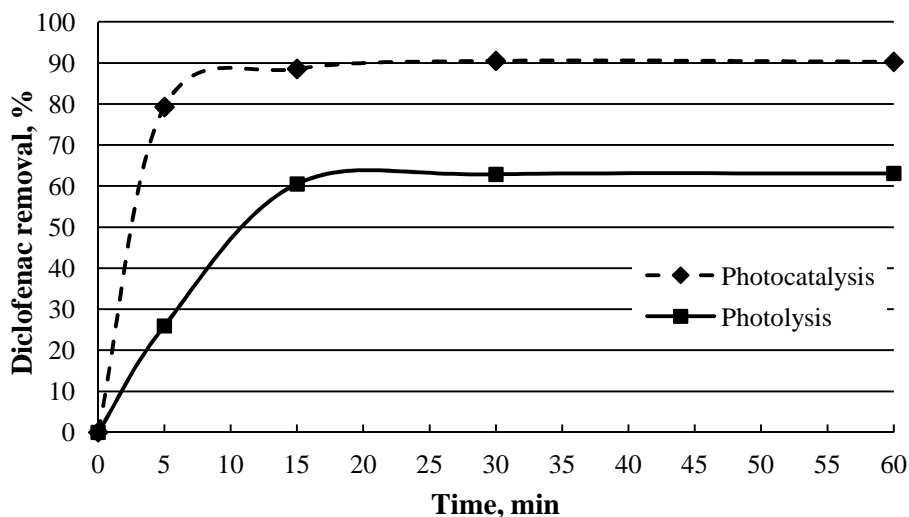


Fig. 2. The decrease of diclofenac concentration during the photolysis and photocatalysis

UV absorbance measurements of the treated water confirmed the photocatalytic decomposition of the investigated pharmaceutical (Fig. 3). The decomposition rates determined on the basis of this analytical method were lower than ones obtained during the chromatographic analysis. 74% reduction of diclofenac concentration was observed at the exposure time of 30 min. The differences in the removal rates of the investigated pharmaceutical obtained during chromatographic analysis and the absorbance measurements resulted of a higher sensitivity of chromatography. The chromatographic method enabled also an unambiguously determination of the investigated drug concentration.

The concentration of total organic carbon was also determined in the treated water after photocatalysis. The values of the parameter decreased by 5 to 35%, depending on the photocatalysis reaction time (Fig. 4). The obtained results indicated on a significant contamination of the water with organic substances. As the decrease of the diclofenac concentration was confirmed with the use of chromatographic analysis, it was assumed that the contamination of the sample was related to the presence of oxidation by-products. Therefore, the measurement of total organic carbon did not only show the decrease of the diclofenac concentration, but also it revealed the presence of by-products formed during the photocatalysis of the investigated compound.

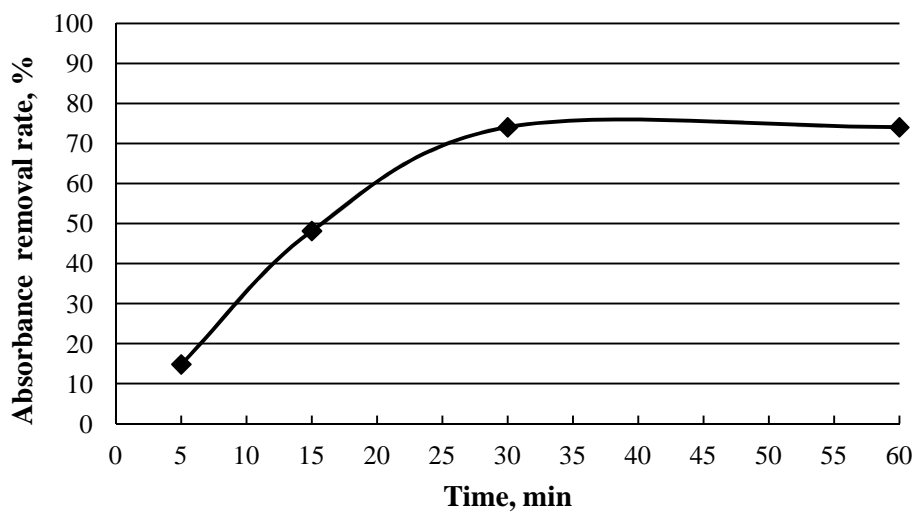


Fig. 3. The decrease of diclofenac during the photocatalysis process based on the UV absorbance removal rate

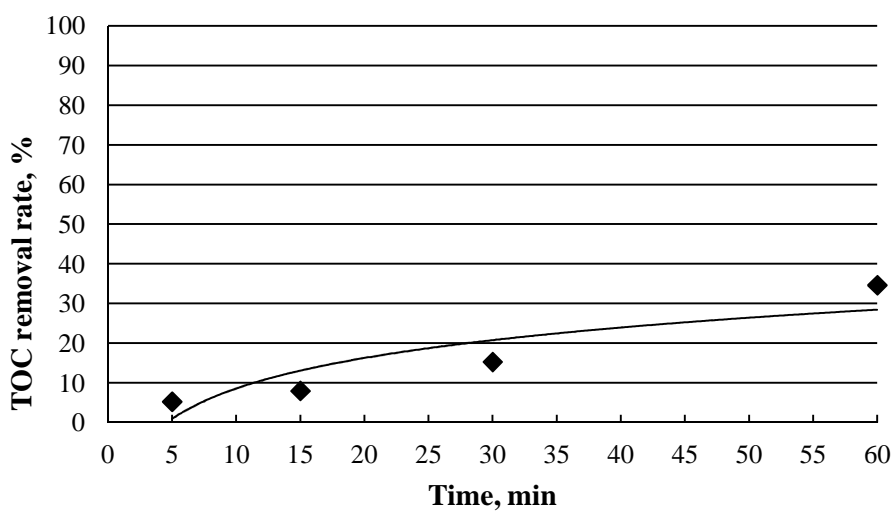


Fig. 4. The dependence of total organic carbon concentration on photocatalysis time

4. CONCLUSIONS

In the paper it was shown that for the complete analytical control of diclofenac concentration during the photocatalytic oxidation number of instrumental

methods had to be used. Chromatographic analysis was found to be useful in order to determine the change of the pharmaceutical concentration. The results of the chromatographic analysis were comparable with ones of the UV absorbance measurements ($\lambda = 276$ nm). Although, the chromatographic measurements revealed the higher sensitivity than the absorbance ones. On the other hand, the total organic carbon analysis showed that the degradation of the removed compound was incomplete and by-products were formed during the process. However, for their identification it is necessary to continue the study with the use of more accurate analytical methods e.g. the GC-MS analysis.

REFERENCES

1. Buntner D., Żabczyński S., Miksch K.: *Usuwanie farmaceutyków ze ścieków*, Chemik, **60**, 2 (2007) 120-124.
2. Carlsson C., Johansson A.K., Alvan G., Bergman K., Kuhler T.: *Are pharmaceuticals potent environmental pollutants?: Part I: Environmental risk assessments of selected active pharmaceutical ingredients*, Science of the Total Environment **364**, 1-3 (2006) 67-87.
3. Chatzitakis A, Berberidou C, Paspaltsis I, Kyriakou G, Sklaviadis T, Poullos I.: *Photocatalytic degradation and drug activity reduction of chloramphenicol*, Water Research, **42**, 1-2 (2008) 386-94.
4. Doll T.E, Frimmel F. H.: *Kinetic study of photocatalytic degradation of carbamazepine, clofibric acid, iomeprol and iopromide assisted by different TiO₂ materials determination of intermediates and reaction pathways*, Water Research, **38**, 4 (2004) 955-964.
5. Fent K., Weston A. A., Caminada D.: *Ecotoxicology of human pharmaceuticals*, Aquatic Toxicology **76**, 2 (2006) 122-159.
6. Heberer T.: *Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data*, Toxicology Letters, **131**, 1-2 (2002) 5-17.
7. Kaniou S, Pitarakis K, Barlagianni I, Poullos I.: *Photocatalytic oxidation of sulfamethazine*, Chemosphere, **60**, 3 (2005) 372-380.
8. Nawrocki J.: *Uzdatnianie wody: procesy fizyczne, chemiczne i biologiczne, Część 1*, Warszawa, Wydawnictwo Naukowe PWN 2010.
9. Salgado R., Pereira V.J., Carvalho G., Soeiro R., Gaffney V., Almeida C., Vale Cardoso V., Ferreira E., Benoliel M.J., Ternes T.A., Oehmen A., Reis M.A.M., Noronha J.P.: *Photodegradation kinetics and transformation products of ketoprofen, diclofenac and atenolol in pure water and treated wastewater*, Journal of Hazardous Materials, **244 - 245**, (2013) 516 -527.
10. Schröder H. Fr., Tambosi J. L., Sena R. F., Moreira R. F. P. M., José H. J., Pinnekamp J.: *The removal and degradation of pharmaceutical compounds*

- during membrane bioreactor treatment, *Water Science & Technology*, **65**, 5 (2012) 833-839.
11. Snyder S.A., Westerhoff P., Yoon Y., Sedlak D.L.: *Pharmaceuticals, personal care products, and endocrine disruptors in water: implications for the water industry*, *Environmental Engineering Science*, **20**, 5 (2003) 449-469.
 12. Ternes T.A.: *Occurrence of drugs in German sewage treatment plants and rivers*, *Water Research*, **32**, 11 (1998) 3245–3260.
 13. Ternes, T.A., Bonerz, M., Hermann, N., Teiser, B., Andersen, H. R.: *Irrigation of treated wastewater in Braunschweig, Germany: an option to remove pharmaceuticals and musk fragrances*, *Chemosphere*, **66**, 5 (2007) 894–904.

KONTROLA ANALITYCZNA USUWANIA DIKLOFENAKU W PROCESIE FOTOKATALITYCZNEGO UTLENIANIA

Streszczenie

Stale rosnąca konsumpcja farmaceutyków przyczynia się do zwiększenia ich stężenia w środowisku wodnym, które kształtuje się na poziomie od kilku ng/dm^3 do kilku $\mu\text{g/dm}^3$. Liczną grupę wśród farmaceutyków występujących w wodach powierzchniowych stanowią niesteroidowe leki przeciwbólowe i przeciwzapalne, do których należy m.in. diklofenak. W pracy przedstawiono możliwości kontroli analitycznej procesu fotokatalitycznego utleniania diklofenaku w środowisku wodnym. Do badania skuteczności procesu zastosowano różne metody instrumentalne, w tym analizę HPLC poprzedzoną ekstrakcją do fazy stałej oraz pomiar przewodności właściwej, absorbancji w UV ($\lambda=276$ nm) i ogólnego węgla organicznego. W celu określenia obniżenia stężenia usuwanego związku przydatna okazała się analiza chromatograficzna, z którą w dobrym stopniu korespondowały wyniki pomiarów absorbancji w UV. Dowiedziono, że pomiar chromatograficzny charakteryzuje się większą czułością niż pomiar absorbancji wody. Na podstawie pomiarów ogólnego węgla organicznego określono, że degradacja usuwanego związku nie jest kompletna i powstają produkty uboczne tego procesu.