

ANALYTICAL CONTROL OF DICLOFENAC REMOVAL IN THE PHOTOCATALYTIC OXIDATION PROCESS

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Abstract

The increasing consumption of drugs results in a continuous release of these chemicals and their metabolites in the aqueous environment, which is at the level of a few ng/dm^3 to several $\mu\text{g}/\text{dm}^3$. Particular attention should be paid to the group of medicines which are available without prescription which include non-steroidal painkillers and anti-inflammatory drugs. 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 the HPLC analysis preceded with solid phase extraction SPE, measurements of UV absorbance and total organic carbon were used. The chromatographic measurements revealed the higher sensitivity than the UV absorbance measurements ($\lambda = 276 \text{ nm}$). 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.

Streszczenie

Stale rosnąca konsumpcja farmaceutyków przyczynia się do zwiększenia ich stężenia w środowisku wodnym, które kształtuje się w zakresie od kilku ng/dm^3 do kilku $\mu\text{g}/\text{dm}^3$. 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 analizę HPLC poprzedzoną ekstrakcją do fazy stałej oraz pomiar absorbancji w UV ($\lambda=276 \text{ nm}$) i ogólnego węgla organicznego. W celu określenia 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.

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 in the group of the antropogenic organic micropollutants [1,2].

These compounds represent a potential risk to aquatic ecosystems, and thus for human health [2,3]. The increasing consumption of drugs results in a continuous release of these chemicals and their metabolites in the environment. 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 [4,5]. The concentration of pharmaceutical compounds in water environment is of a few ng/dm^3 to several $\mu\text{g/dm}^3$ and depends on the load of 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 [6,7] 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 [8-10].

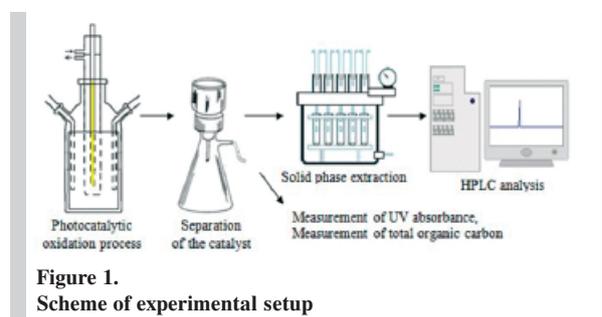
Advanced water treatment technologies which include among others membrane techniques - nanofiltration and reverse osmosis [11] and advanced oxidation processes - ozonation [12] and photocatalytic oxidation [13-17] are an alternative to the commonly used sorption and coagulation processes or biologically active carbon filters for surface water treatment. 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 UV wavelength is possible based 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 by-products can reduce the final treatment effect. Thus, only a reduction of the initial compound concentration is observed, opposite to its degradation pathway.

The paper presents the possibility of analytical control of diclofenac removal from water solutions 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 (TiO_2) by Evonik Degussa (Germany) marked with the symbol P25 was used as catalyst. Methanol, acetonitrile and water for HPLC supplied by POCH S.A. were also used in the study. SPE Supelclean™ ENVI-8 tubes of a volume of 6 cm^3 (1.0 g) by Supelco and a SPE chamber also by Supelco were used during the solid phase extraction. The photocatalytic oxidation process was carried out in a laboratory batch reactor (Heraeus) equipped in an immersed medium pressure lamp of 150 W placed in a cooling jacket, which ensured the maintenance of a constant process temperature of 20°C . To aerate the water in the reactor during the photocatalytic process a aeration pump with a capacity of 0.25 cm^3 air for 1h was used. The separation of the catalyst from the reaction mixture were carried out by the use of a filtration set connected to a vacuum pump from AGA Labor equipped with glass fiber filters ($0.45\ \mu\text{m}$) by Millipore.



2.2. Research methodology

In the study, the simulated solutions were prepared on deionized water matrix, to which diclofenac in a constant concentration of 1 mg/dm^3 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 50 mg/dm³ of the catalyst (TiO₂) underwent the photocatalytic oxidation process at different times i.e. 5, 10, 15, 30, 45 and 60 min.

In the preliminary study, based on the data regarding the efficiency of diclofenac removal in the sorption process on TiO₂ catalyst, the optimal contact time between the catalyst and the water test samples before the beginning of the photocatalytic oxidation process was determined. The sorption was carried out for 60 min.

2.3. Analytical methods

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),
- 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 5 cm³ 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 column 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 chromatography 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 – 5 μ m. The mobile phase consisted of a mixed water and acetonitrile in the ratio of 85:15 (v/v).

The separation efficiency and its precision (expressed by the average standard deviation, %) were determined based on results obtained for four extractions. It was found that the extraction yield of diclofenac

was 85% and the precision of determination between individual samples did not exceed 1%.

In the preliminary work the diclofenac maximum absorbance ($\lambda_{\text{max}} = 276$ nm) was identified from a designated UV-VIS spectra registered using the UV-VIS spectrophotometer Cecil 1000 by Jena AG for the wavelength range from 200 to 400 nm (Fig. 1).

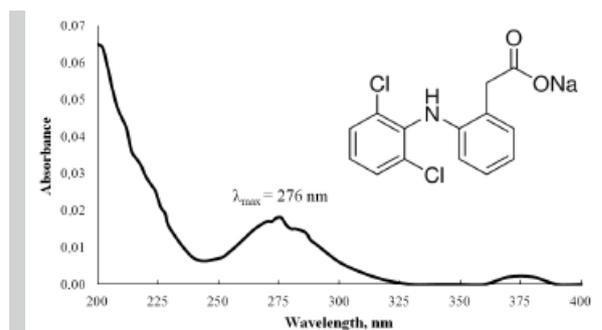


Figure 2. UV-VIS spectrum of diclofenac and its chemical structure

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

Before the photocatalytic oxidation process of diclofenac, the efficiency of its removal in the sorption process on the TiO₂ catalyst was determined with the use of HPLC analysis, which was preceded by solid phase extraction SPE. The sorption was carried out for 60 min. After 15 min the drug concentration in the tested water sample decreased by more than 19% as a result of drug particles adsorption on the surface of the photocatalyst. The extension of the contact time of the water test sample with TiO₂ particles does not increase the removal degree of diclofenac.

In the following stages of research a 15 min contact time of the photocatalyst with the water test sample before light exposure took place.

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 favoured 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.

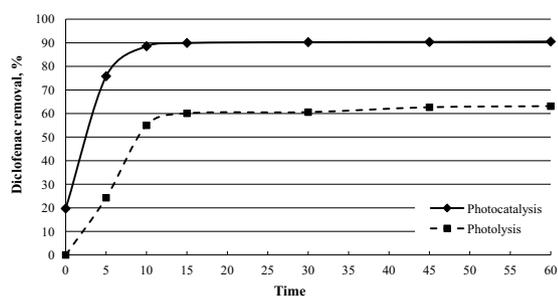


Figure 3.
The decrease of diclofenac concentration during the photolysis and photocatalysis

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 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 from a higher sensitivity of chromatography. The chromatographic method enabled also an unambiguous determination of the investigated drug concentration.

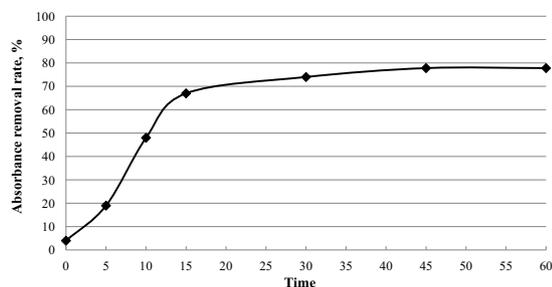


Figure 4.
The decrease of diclofenac during the photocatalysis process based on the UV absorbance removal rate

The concentration of total organic carbon was also determined in the treated water after photocatalysis. The values of the parameter decreased by 18 to 28%, depending on the photocatalysis reaction time (Fig. 4). The obtained results indicated 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.

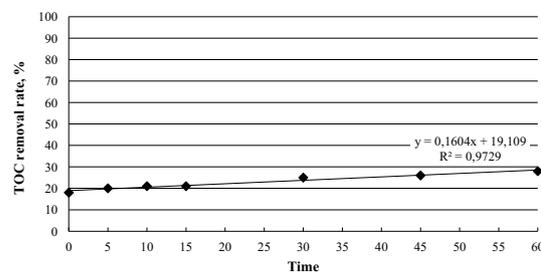


Figure 5.
The dependence of total organic carbon concentration on photocatalysis time

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.

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