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Influence of the catalyst type (TiO_2 and ZnO) on the photocatalytic oxidation of pharmaceuticals in the aquatic environment

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ABSTRACT

In recent years, an increasing interest in the new group of contaminants appearing in the aquatic environments i.e. pharmaceuticals and personal care products has been observed. The effect of the long-term exposure of living organisms to sufficiently lower the concentration of pharmaceuticals, which are found to be highly reactive, is still unknown. In addition with no toxicological data of pharmaceuticals action on living organisms, including humans, their constant elimination from water dedicated to human consumption is required. In this article, the efficiency of chosen pharmaceutical compounds via photocatalysis process is discussed. The photolysis process was also performed in order to compare both solutions. Titanium dioxide (TiO_2) and zinc oxide (ZnO) were used as catalysts. The photocatalytic process was also evaluated according to the toxic effect of the purified water by means of MICROTOX® analysis. The impact of the pharmaceutical concentration and oxidation time on the water samples toxicity has also been investigated. The highest efficiency of the process was revealed at the presence of TiO_2. The removal rate of pharmaceutical compounds reached 90%. It was additionally found that the radiation of water containing ZnO resulted in the generation of toxic byproducts, which significantly decreased the quality of purified water.

Keywords: Pharmaceutical compounds; Photocatalysis; Oxidation by-products; Toxicity

1. Introduction

One of the most important topics of the protection and quality improvement of water environment is the determination of micro-pollutants emission sources and the establishment of their concentrations in the environment as well as the development of the methods used for their complete elimination. In recent years, an increasing interest in the new group of micro-pollutants, which appear in the environment, known as pharmaceutical and personal care products, has been observed [1–4]. The main source of pharmaceutical compounds and their metabolites in the water environment are effluents from wastewater treatment plants [3].

Pharmaceuticals get to the wastewater stream with human and animal feces as they are only partially

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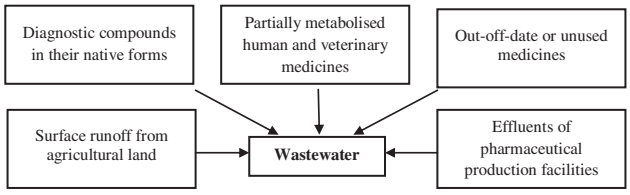


Fig. 1. Pathways of wastewater contamination with pharmaceuticals [5].

metabolized in their organisms [5]. Other pathways of pharmaceuticals migration to wastewater streams are shown in Fig. 1. The concentration of particular micropollutants in water depends on their load introduced to the natural collector together with the treated wastewater. Usual concentration levels are in the range from only a few ng/dm^3 up to several μg/dm^3.

Among pharmaceuticals the most commonly met in the water environment diclofenac (DCL) and ibuprofen (IBU)—non-steroidal and anti-inflammatory drugs, as well as carbamazepine—psychotropic medicine, are to be found. The environmental concentration of those drugs is 1.3 μg/dm^3 for DCL [6], 1 μg/dm^3 for IBU [7], and from 0.02 to 2 μg/dm^3 for carbamazepine [8,9].

Pharmaceuticals as chemical compounds of significant stability possess potential negative impact on ecosystems and biologically affect living organisms depending on their specificity [10]. Non-steroidal anti-inflammatory medicines are weak acids, which cause reversible or irreversible blockage of one of the cyclooxygenase isoforms i.e. the enzyme which participates in the synthesis of prostaglandin from arachidonic acid [11]. In the study carried out by Schwaiger et al. [12] and Triebskorn et al. [13] on rainbow trout (*Oncorhynchus mykiss*) the 28 d long exposition to DCL at 1 μg/dm^3 concentration caused changes in kidneys, liver, and gills. The study on salmon trout (*Salmo trutta* m. *fario*) showed the same effect, but already after 21 d of exposition at lower 0.5 μg/dm^3 DCL concentration [14]. Moreover, a toxic effect of DCL on phytoplankton (EC_{50} = 14.50 mg/dm^3) and zooplankton (EC_{50} = 22.43 mg/dm^3) [15] after 96 h of exposition was revealed. IBU is another pharmaceutical that shows chronic toxicity. The exposure of Japanese rice fish (*Oryzias latipes*) to various medicine concentration for 6 weeks has resulted in a significant liver weight increase, intensive eggs production, and decreased number of spawns per week [16]. The same pharmaceutical at concentration ranges from 1 to 10 ng/dm^3 resulted in a decrease in amphipod *Gammarus Pulex* activity [17]. In the case of photosynthetic water organisms the stimulation of cyanobacteria *Synechocystis* sp. growth after 5 d of exposure at IBU concentration range from 1 to 1,000 μg/dm^3 was observed, while simultaneously the limitation of *Lemna minor* growth after 7 d of exposure was observed [18]. During the toxicity tests carried out by Ferrari et al. [19] on freshwater Crustaceans (*Ceriodaphnia dubia)* exposed for 7 d to carbamazepine the NOEC concentration equal to 25 μg/dm^3 has been determined. However, there is no information about the toxic effect of pharmaceuticals present in water environment on humans. Thus, the complete elimination of this group of micro-pollutants from water dedicated to human consumption has become a must. However, technological lines of wastewater plants based only on biological processes do not guarantee the effective removal of pharmaceuticals according to both, polar structure of compounds and biochemical degradation resistance.

The complete elimination of pharmaceuticals from aquatic streams is very problematic. Zwiener and Frimmel observed only 4% removal of DCL during activated sludge treatments (the sludge was collected at "Karlsruhe wastewater treatment plant", Germany) in their studies [20]. Yu et al. [21] investigated the effluent from Baltimore wastewater treatment plant and found only 18% removal rate of DCL. In the case of carbamazepine, the activated sludge wastewater treatment enabling its removal rate does not exceed 10% [22–24]. However, Paxeus [25] observed an increased removal of carbamazepine equal to 53%, at the present, of oily substances in the wastewater, which are able to extract the pharmaceutical from the aquatic stream. In the classification scheme of pharmaceuticals on their susceptibility to biodegradation carbamazepine is found as non-biodegradable [26].

Advanced oxidation processes (AOPs) are found to be an interesting alternative for typical treatment methods [25]. Oxidizing agents involved in this processes are free radicals, especially hydroxyl ones ($OH^{\cdot}$), which characterize with very high redox potential (2.8 V) that enables fast and non-selective oxidation of organic compounds. The effect of hydroxylation and dehydroxylation processes is the complete mineralization of organic substances to CO_2 and H_2O [26]. The most commonly used AOPs are photolysis, ozonation, Fenton reaction, UV radiation, heterogenic photocatalysis with semiconducting catalysts, sonolysis, radiolysis, and a series of other electric and electrochemical methods.

There are two main types of photocatalysis process: homogeneous one, in which the catalyst appears in the same phase as a substrate (e.g. both of them are dissolved) and heterogeneous one. In the latter case, the process run at the boundary of two phases i.e. solid photocatalyst phase and aqueous or gaseous polluted phase. As the most popular catalysts used metal oxides e.g. TiO_2, ZnO, SnO_2, or sulfides—ZnS and CdS are to

be mentioned [27–29]. Among those the most commonly used semiconducting photocatalyst is titanium dioxide (TiO_2), as a mixture of anatase and rutile. The first step of photocatalysis reaction is the excitation of the photocatalyst particle with quantum of light. The excitation is the result of the radiation of the semiconductor, which possesses the energy equal or higher than the band gap energy of the semiconductor. In the case of TiO_2, the energy should be 3.2 eV I for anatase and 3.0 eV for rutile [30,31]. The absorbed photon causes the transportation of the electron from the low-energy valence band to the high-energy conduction band, where the formation of electron–electron gap pairs occurs. It starts the chain of redox reductions during which organic contaminants are decomposed [32–34].

In this paper, the efficiency of removal of chosen pharmaceutical compounds during photocatalysis process is discussed. The photolysis process was also investigated as the comparative one. TiO_2 and zinc oxide (ZnO) were used as catalysts. The photocatalysis process was also evaluated according to the toxic effect of purified water using MICROTOX® analysis. The impact of the pharmaceutical concentration and oxidation time on samples toxicity was investigated. The kinetics of the photocatalysis was described using Langmuir–Hinshelwood model.

2. Material and methods

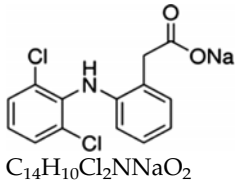
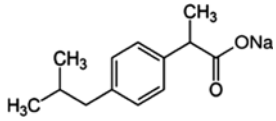
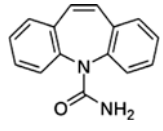
2.1. Material and reagents

The standards of both, psychotropic medicines i.e. carbamazepine (CBZ) and non-steroidal analgesics and anti-inflammators in the form of sodium salts of DCL and IBU of purity grade >98% were supplied by Sigma-Aldrich (Table 1). The same company supplied ZnO catalyst, while in the case of (TiO_2) a commercial product P25 supplied by Degussa was used. In the study, methanol and acetonitrile of purity grade >99.8% and >99.5%, respectively, by POCH were also used. Disposable Supelclean™ ENVI-8 columns of volume 6 cm^3 (1.0 g) by Supelco were applied to solid phase extraction (SPE). Details of the method are presented in the reference [35].

2.2. Photolysis and photocatalysis

Both, photolysis (UV) and photocatalytic oxidation processes were carried out in the laboratory batch reactor Heraeus (volume of 700 ml) equipped with medium-pressure, an immersed, mercury lamp of power 150 W placed in the cooling jacket made of the special glass Duran 50, which enabled the blockage of radiation of wavelength <300 nm. The lamp cooling assured the constant process temperature equal to 20±1°C. The aeration of the reactor was based on an aeration pump of capacity 0.25 cm^3 of air per 1 h. This capacity was sufficient for the proper execution of a photocatalysis process. The oxygen supplied to the reactor also holds catalyst particles in the suspended state at the whole reactor volume and prevents the recombination phenomena [36]. The radiation was carried out constantly for 60 min. The dose of each catalyst (TiO_2 or ZnO) introduced into the water sample containing a mixture of pharmaceutical compounds was equal to 50 mg/dm^3 The photocatalyst dose was selected during the preliminary stage of the study. The contact time of the catalyst with treated water before its irradiation was established at 15 min. The separation of the catalyst from the treated solution was made with the use of the filtration set which comprised of glass fiber filter (0.45 μm) by millipore, which was connected to the vacuum pump AGA Labor.

Table 1
The structural and chemical characteristics of investigated pharmaceuticals

Pharmaceutical compound	DCL sodium salt	IBU sodium salt	Carbamazepine
Structural formula			
Molecular formula	$C_{14}H_{10}Cl_2NNaO_2$	$C_{13}H_{17}O_2Na$	$C_{16}H_{12}N_2O$
Molecular weight (g/mol)	318.13	228.26	236.3
Solubility in water (mg/$cm^{3)}$	50	100	0.17
pK_a	4.15	4.91	2.3
log K_{ow}	4.51	3.97	2.45

2.3. Water samples

In the study, water solutions prepared on deionized water matrices with the addition of DCL, IBU, and carbamazepine standards of concentrations 0.5, 1, 2, and 5 mg/dm^3. The high concentration of medicines i.e. much higher than the one occurring in the environment was used in order to increase the precision of the performed analytical measurements. The concentrations of pharmaceuticals were selected also taking into account their solubility in water. Thus, in the case of all investigated pharmaceuticals, including CBZ, were well dissolved in water. The pH of the solutions was adjusted to 7 using 0.1 mol/dm^3 HCl and 0.1 mol/dm^3 NaOH.

Firstly, photolysis of simulated water solution was performed. Next, the photocatalysis preceded with photocatalysts addition was carried out at various times i.e. 5, 10, 15, 30, 45, and 60 min.

2.4. Analytical procedure

The analytical procedure of investigated pharmaceutical compounds was performed according to the following methodology:

- the extraction of pharmaceuticals from water phase by means of SPE,
- the quantitative–qualitative analyses of pharmaceuticals using high performance liquid chromatography (HPLC) and UV chromatography.

The HPLC analysis was preceded with the solid phase extraction (SPE) of analyzed water samples of volume 20 cm^3 (pH 7) using columns filled with octylsilane bed (C_8). The bed was firstly washed with 5 cm^3 of methanol and next conditioned with 5 cm^3 of deionized water of pH 7. After the column preparation, the investigated water solution was introduced on the column. When the extraction was finished, the bed was dried for 5 min under vacuum. The extract was next eluted with 3 cm^3 of methanol, dried with nitrogen stream, dissolved in 100 μl of methanol, and directed to the chromatographic analysis.

The chromatographic procedure was performed using HPLC by Varian (UV detector, wavelength $\lambda = 220$ nm) equipped with Hypersil GOLD column by Thermo Scientific of length 25 cm, diameter 4.6 mm, and graining 5 μm. The mixture of acetonitrile and water in the volume ratio of 85:15 (v/v) was the mobile phase. The injection was the manual using microsyringe by Hamilton of volume 50 μl.

Every extraction of standards dissolved in deionized water was repeated four times in order to determine the precision of the process (expressed as mean standard deviation, %). It was found that the capacity of SPE reached 85% and differences in the analysis of particular samples did not exceed 9%. It confirmed that the precision of the method was satisfying.

2.5. Photolysis and photocatalysis process kinetics

The interpretation of photolysis and photocatalysis processes kinetics was obtained using Langmuir–Hinshelwood [37] equation as a conjugated function of pharmaceuticals concentration and time:

$$r = \frac{dC}{dt} = k\left(\frac{KC}{1 + KC}\right) \tag{1}$$

where k—reaction rate constant, 1/min; r—rate of reaction, mg/dm^3 min; K—organic compounds adsorption equilibrium constant; C—concentration of organic compounds at any time t during degradation, mg/dm^3.

Assuming that the oxidation of pharmaceutical compounds during photocatalysis is pseudo-first-order reaction, the reaction rate constant can be calculated by Eq. (2) [37]:

$$-\ln\left(\frac{C_0}{C_t}\right) = kt \tag{2}$$

where k—reaction rate constant, 1/min; t—reaction time, min; C_0—initial concentration of organic compounds, mg/dm^3; C_t—concentration of organic compounds at time t during the degradation, mg/dm^3.

The half-life $t_{\frac{1}{2}}$ of investigated compounds was determined using Eq. (3):

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k} \tag{3}$$

2.6. Toxicity test

In toxicity measurements MICROTOX® test with bioluminescence bacteria *Vibrio fisheri* characterized with high sensitivity to a wide spectrum of toxic substances was used [38]. During the exposure of indicating micro-organisms to toxic substances either the metabolic changes occur or a decrease in population is observed and, as a consequence, it leads to the change in the intensity of light emitted by bacteria [39].

Those tests were carried out according to the screening test procedure of MicrotoxOmni system in

Microtox analyzer Model 500, which acted as both, an incubator and a photometer. The rate of bioluminescence inhibition in reference to the control sample (bacteria unexposed to the toxicant action) was measured after 5 and 15 min of the exposure.

3. Results and discussion

3.1. Photolysis

The photolysis process was carried out for water solutions containing investigated compounds (DCL, IBU, and CBZ) independently. The impact of the concentration of the given compounds on its removal effectiveness was checked. Four concentrations of micro-pollutants i.e. 0.5, 1, 2, and 5 mg/dm^3 were applied. The obtained results are presented graphically in Fig. 2. It was found that the concentration of investigated micro-pollutants decreased with UV time. The parameter depended on the initial compound concentration. A similar dependence was also observed in Rizzo et al. [40] and Im et al. [41] studies. The decomposition rate of DCL after 60 min of radiation with its initial concentration increase in the solution was 80 (initial concentration 0.5 mg/dm^3), 63 (1 mg/dm^3), 62 (2 mg/dm^3), and 61% (5 mg/dm^3). Decomposition rates obtained for other compounds at the lowest initial concentration were at the same level. In the case of IBU concentrations being equal to 2 and 5 mg/dm^3 only 20% removal was observed. The lowest removal rate equal to 6% was noted for CBZ at concentration of 5 mg/dm^3. Similar results are shown in [41]. Such high concentrations of CBZ are observed only in the case of hospital wastewater [42]. Thus, UV process was found to be ineffective in the case of such high concentrations of pharmaceuticals. The introduction of the catalyst to the system seems to be a good solution and it was discussed in the further part of the paper.

In Table 2 half-lives of investigated pharmaceuticals and reaction rates determined on the basis of Langmuir–Hinshelwood model are presented. The kinetic determination was made for time range from 0 to 30 min.

The obtained results show that the rate of photolytic oxidation decreases with an increase in the pharmaceutical initial concentration. The highest values of the parameter were obtained for DCL. On the other hand, half-lives of pharmaceutical elongated with an increase in the concentration. The parameter values observed for IBU and CBZ at the initial concentration of 5 mg/dm^3 were 22 and 50 times greater, respectively, that the half-life of DCL at the same initial concentration.

3.2. Photocatalysis

The next part of the study was focused on the evaluation of the impact of the presence of photocatalyst on the decrease in pharmaceuticals concentration at irradiation with UV light. Firstly, the effectiveness of photocatalysis with TiO_2 at the dose 50 mg/dm^3 (Fig. 3) was investigated. During the preliminary stage of the process, the efficiency of adsorption of investigated compounds on the photocatalyst surface was checked. The contact time was equal to 15 min. The procedure was applied in order to accurately distribute the catalyst in the total volume of water and to initiate the adsorption process on the semiconductor nanoparticles. The concentration of DCL had already decreased by 19% as a result of the adsorption, regardless of the initial concentration of the compound. In the case of IBU, the adsorption rate increased with the initial increase in concentration i.e. from 19% (initial concentration 0.5 mg/dm^3), 37% (1 mg/dm^3), 57% (2 mg/dm^3) to 57% (5 mg/dm^3). Opposite behavior was observed for CBZ. At the initial concentration 0.5 mg CBZ/dm^3 the adsorption rate reached almost 15%, while at 5 mg CBZ/dm^3 it was only 0.2%. Hence, the impact of chemical character of the compounds on the adsorption process was revealed. It can be supposed that in the case of weak acids (IBU and DCL) the adsorption rate is constant or increases with their concentration increase in water, while the opposite tendency is observed for compounds from the amide group.

The photocatalytic oxidation resulted in much more efficient removal of pharmaceuticals than photolysis process. The effectiveness of compounds mineralization increased with the reaction time elongation. The removal rate of non-steroidal pharmaceuticals i.e. IBU and DCL increased with the initial concentration increase. The dependence was especially noticeable in the case of IBU. The removal rates noted for this compound after 30 min of the process decreased by 76% (concentration 0.5 mg/dm^3), 80% (1 mg/dm^3), 88% (2 mg/dm^3), and 89% (5 mg/dm^3). The concentration of DCL measured after 30 min of the process at the lowest medicine concentration decreased by 56%, while in the case of other concentrations the removal rate always exceeded 90%. In the case of photocatalytic decomposition of compounds with rather weak acidic character the formation of H^+ ions responsible for a decrease in the reaction environment pH takes place. The surface of TiO_2 particles at pH ranges above the isoelectric point i.e. the point at which the total charge of TiO_2 is equal to 0 (pH_{pzc}), becomes positively charged. It results in the intensification of the adsorption of pharmaceuticals which possess negative charge on the catalyst surface,

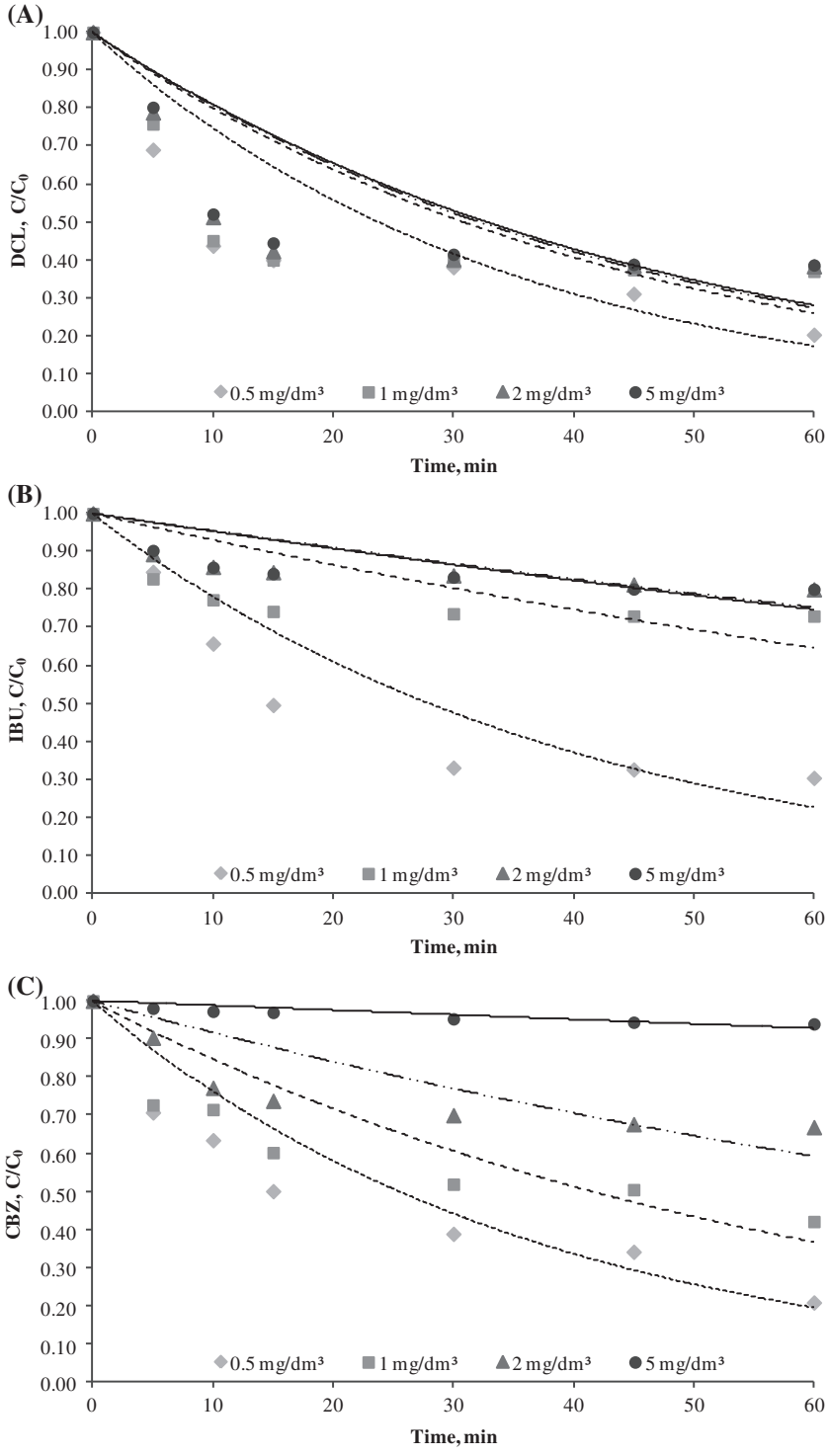


Fig. 2. Change of pharmaceuticals (DCL—A, IBU—B, CBZ—C) during photolysis.

and consequently their removal rate increases. It is known that the effectiveness of the photocatalysis depends on the adsorption rate of compounds on the catalyst surface.

Table 2
Decomposition half-lives of investigated pharmaceuticals obtained for the photolysis process

Pharmaceutical	Concentration (mg/dm^3)	Reaction rate constant k (min^{-1})	R^2	Half-life $t_{\frac{1}{2}}$ (min)
DCL	0.5	0.0642	0.86	10.4
	1	0.0624	0.89	11.2
	2	0.0591	0.95	11.7
	5	0.0548	0.93	12.2
IBU	0.5	0.0367	0.97	17.6
	1	0.0041	0.67	119.7
	2	0.0022	0.71	260.8
	5	0.0021	0.69	276.9
CBZ	0.5	0.0205	0.97	19.9
	1	0.0096	0.93	41.0
	2	0.0087	0.72	65.2
	5	0.0011	0.98	616.4

The opposite behavior was observed for carbamazepine, which removal rate decreased with the initial concentration increase, as it was also observed during photolysis process. The conductance of the photocatalysis for 60 min resulted in the CBZ removal rate at the level of 82% (initial concentration 0.5 mg/dm^3), 68% (1 mg/dm^3), 50% (2 mg/dm^3), and 12% (5 mg/dm^3).

Half-lives of particular pharmaceuticals and reaction rate constants are shown in Table 3. The determination of those values for IBU concentrations 2 and 5 mg/dm^3 was not possible as 50% removal rate was caused by the compound adsorption on the catalyst surface. The study of the kinetics of DCL and IBU did not show the clear dependence of the reaction rate constant on compounds concentration. Almost five-fold shortening of IBU half-life was observed for an increase in its initial concentration from 0.5 to 1 mg/dm^3. In the case of CBZ, a similar dependence of the reaction rate constant and half-life increase on the concentration increase as in the case of the photolysis was observed.

The photocatalysis process with ZnO at the dose of 50 mg/dm^3 was carried out for simulated waters containing DCL, IBU, or CBZ at the concentration of 1 mg/dm^3. The obtained decomposition rates were lower than the ones observed for titanium dioxide. The results of both types of photocatalysis process were compared in Fig. 4. The decomposition rate of DCL and IBU after 30 min of radiation was equal to 68 and 60%, respectively. The CBZ concentration decreased by 60% after 60 min of the process performance. The higher efficiency of the processes carried out at the presence of TiO_2 was also shown by Haroune et al. [43] and Barents et al. [44]. The catalyst type also had an impact on the half-life elongation, which is shown in Table 4.

3.3. Toxicity

On the basis of the results of MICROTOX® toxicity tests the dependence between water samples toxicity and the concentration of particular pharmaceuticals was evaluated for 5 and 15 min exposure periods (Fig. 5). An increase in micro-pollutants concentration resulted in the more intensive inhibition of bioluminescence, which also indicated on the water toxic effect increase. The parameter decreased insignificantly with the exposure time elongation. Nevertheless, it was found that water solutions containing DCL or IBU revealed some toxic effect on the level of less than 10% at the highest pharmaceuticals concentration. According to the toxicity classification, the water of such characteristics is said to be non-toxic [45]. Water samples containing CBZ at concentrations of 2 and 5 mg/dm^3 were classified as waters of low toxicity (bioluminescence inhibition in the range from 20 to 40%).

Next, the evaluation of the investigated oxidation processes on water toxicity was checked. The irradiation of water containing only TiO_2 or ZnO with no pharmaceuticals was performed. It made it possible to determine the possibility of toxic byproducts for the irradiation of only photocatalysts. In the case of titanium dioxide no toxic effect was observed, whereas already after 5 min of irradiation of water containing ZnO the water toxic effect increase was revealed (Fig. 6). Water samples which underwent irradiation for more than 30 min during the *Vibrio fischeri* 15 min exposure tests were classified as toxic. Such results indicated that the performance of photocatalysis process with ZnO was disadvantageous, and despite its ability to decompose organic compounds, toxic byproducts of the catalyst decomposition were formed.

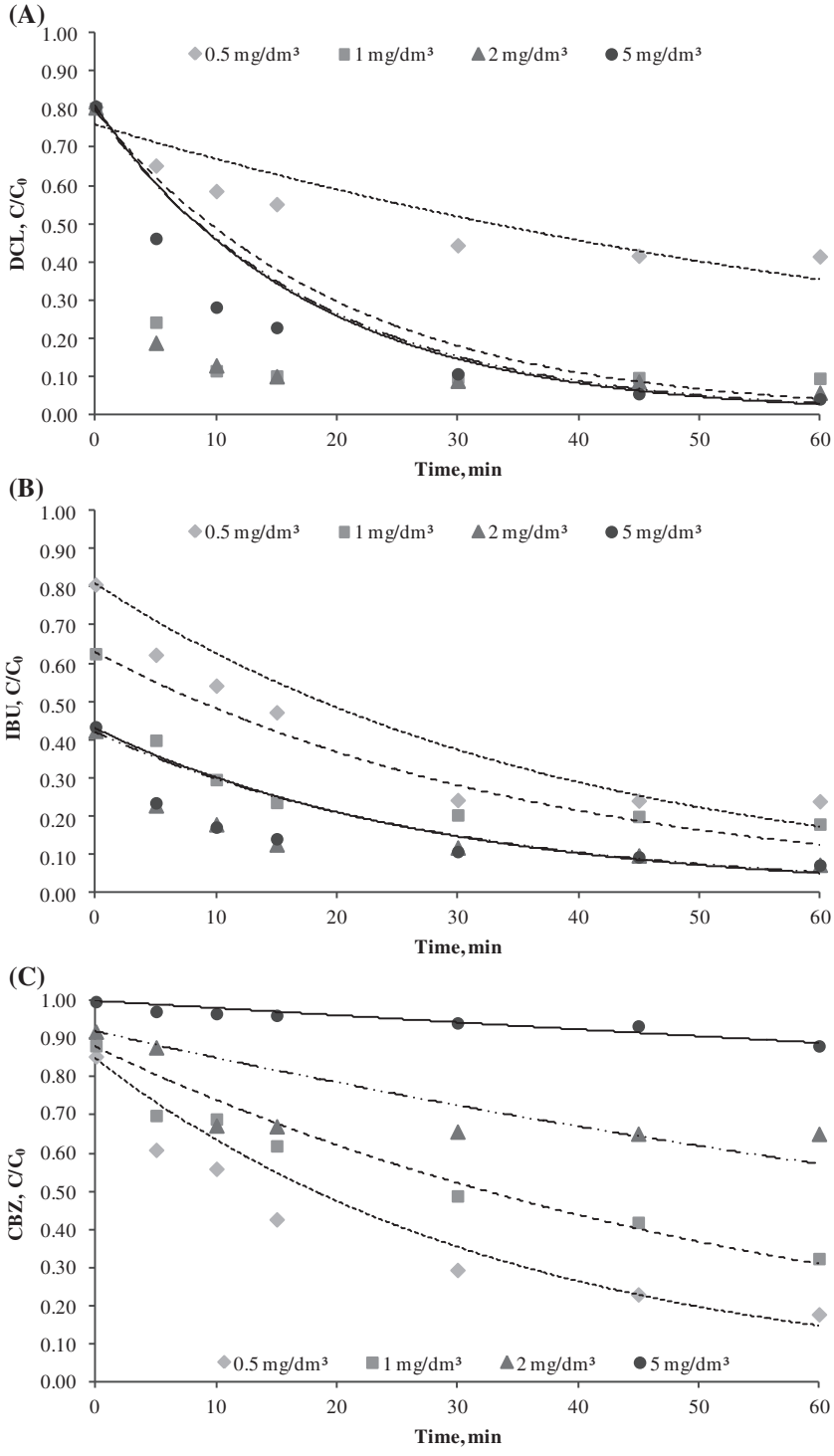


Fig. 3. Change of pharmaceuticals concentrations (DCL—A, IBU—B, CBZ—C) during the photocatalysis with TiO_2.

The changes of toxicity were also analyzed for the pharmaceuticals photocatalysis process with TiO_2 at compounds concentration of 5 mg/dm^3 (Fig. 7). For irradiation times equal to 5, 10, 30, and 60 min the toxic effect of waters containing DCL increased by 17, 39, 30, and 10%, respectively, while for ones with IBU

Table 3
Decomposition half-lives of pharmaceuticals observed during photocatalysis with TiO_2

Pharmaceutical	Concentration (mg/dm^3)	Reaction rate constant k (min^{-1})	R^2	Half-life $t_{\frac{1}{2}}$ (min)
DCL	0.5	0.0185	0.93	21.5
	1	0.1395	0.89	1.5
	2	0.1327	0.84	1.0
	5	0.0647	0.95	4.2
IBU	0.5	0.0391	0.99	11.9
	1	0.0647	0.97	2.5
	2	0.0391	0.74	–
	5	0.0425	0.82	–
CBZ	0.5	0.0341	0.96	12.9
	1	0.0181	0.94	27.6
	2	0.0114	0.64	47.7
	5	0.0017	0.89	400.7

Note: The determination of half-lives was impossible according to the 50% removal rate of compounds already at the adsorption stage.

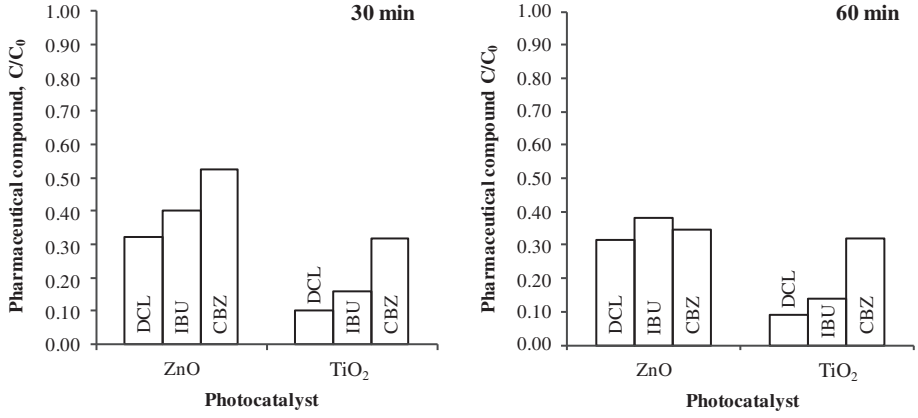


Fig. 4. Decrease in pharmaceutical concentration during the photocatalysis at the presence of ZnO or TiO_2 (30 and 60 min).

Table 4
Decomposition half-lives of pharmaceuticals during the photocatalysis with ZnO

Pharmaceutical	Reaction rate constant k (min^{-1})	R^2	Half-life $t_{\frac{1}{2}}$ (min)
DCL	0.0574	0.98	8.58
IBU	0.0328	0.92	13.04
CBZ	0.0152	0.98	36.45

it was 35, 41, 17, and 1%. Toxic effects determined for water with CBZ at the same irradiation times were 51, 61, 67, and 84%. An increase in the toxicity during the process confirmed the fact that the formation of toxic byproducts of decomposed pharmaceuticals were found to be more toxic than maternal compounds. Oxidation byproducts of IBU and DCL were found to be formed, the most intensively, at the beginning of the process (up to ca. 15 min) and next they also underwent the oxidation, what was indicated by the water toxic effect decrease. In the case of CBZ, an increase in the toxicity was observed within the whole time of the process run. It results mainly of the low CBZ removal rate during the photocatalysis (Fig. 3(C)). In this case, water samples irradiated for more than 30 min were classified as highly toxic.

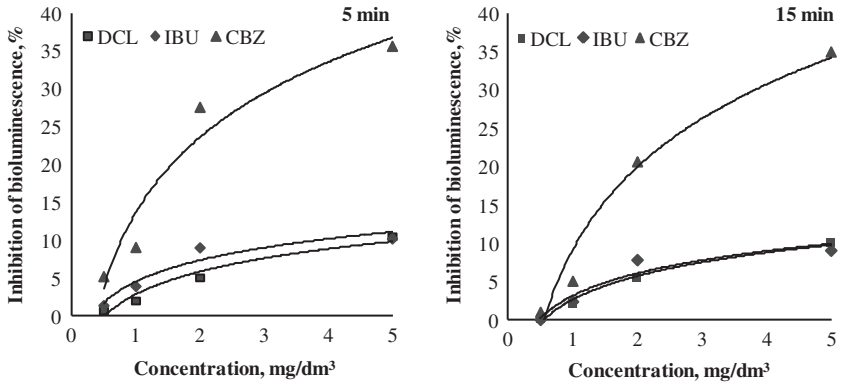


Fig. 5. The dependence of water toxicity level on pharmaceuticals concentrations (the exposure time: 5 and 15 min).

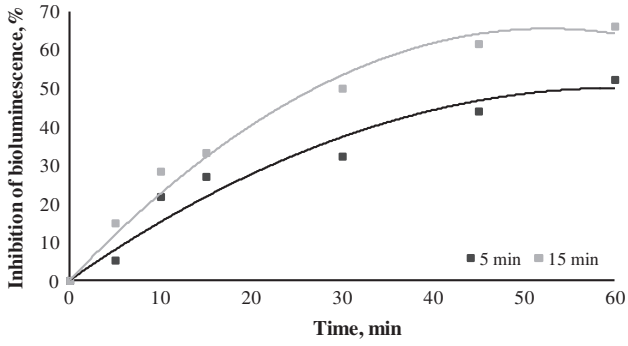


Fig. 6. Changes in water toxicity during the photocatalysis process with ZnO (the exposure time: 5 and 15 min).

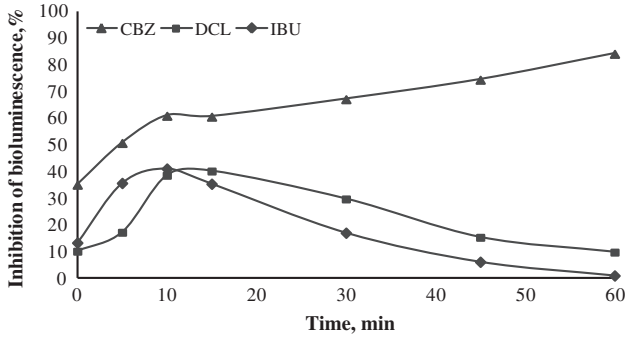


Fig. 7. The change of water toxicity during the pharmaceuticals photocatalysis with TiO_2 (the exposure time: 15 min).

4. Conclusions

The comparative studies results on the effectiveness of chosen pharmaceutical removal via photolysis and photocatalysis with TiO_2 or ZnO showed that the presence of the catalyst had a positive impact on the oxidation of pharmacological micro-pollutants. The effectiveness of the process depended on the initial concentration of the compound and in the case of CBZ it decreased with the concentration increase. The process catalyzed with TiO_2 runs most effectively enabling the removal of DCL to the range of more than 90% at the pharmaceutical initial concentration of 2 and 5 mg/dm^3. The results obtained during the toxicity tests revealed the possibility of oxidation byproducts formation which could have higher toxic effect than one of the maternal compound. Additionally, it was found that the use of ZnO as a catalyst caused an increase in water toxicity according to the catalyst self-decomposition. It indicates on the low applicability of ZnO to water or wastewater treatment.

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