Diclofenac removal from waste water by UV-A LED-based heterogeneous photocatalysis

Vojtěch Trousil[1], Jiří Palarčík[1]*, Marek Smolný[1], Zuzana Blažková[1], Oldřich Machalický[2], and Jiří Cakl[1]

[1] *Institute of Environmental and Chemical Engineering,*
The University of Pardubice, CZ–532 10 Pardubice, Czech Republic

[2] *Institute of Organic Chemistry and Technology,*
The University of Pardubice, CZ–532 10 Pardubice, Czech Republic

Degradation of the active pharmaceutical ingredient diclofenac (DCL) was studied using a laboratory-scale photoreactor equipped with highly efficient UV-A LEDs. Three photocatalysts (Aeroxide P25, Hombikat UV 100 and Precheza AV01) were tested and compared. In addition to deionized water, the other types of water (water matrices), were then tap water, unfiltered surface water, and the primary effluent of a wastewater from the municipal treatment plant. The experimental results indicated that the UV-A LED source operating at a wavelength of 368 nm had been much more efficient when combined with Precheza AV-01 photocatalyst of the microstructured anatase type. A negligible contribution of photolysis was noticed, while UV-A/TiO₂ photocatalysis was more efficient in DCL removal in both the tap and the surface water matrices. The removal rate of DCL from the wastewater matrix was more dependent on the matrix itself than on the chemical structure of the micropollutant. The addition of hydrogen peroxide to the photocatalytic system enhanced the removal rates. The results of the algal growth inhibition test revealed a significant reduction of toxicity to Parachlorella kessleri after UV-A LED irradiation of the DCL solution. In addition, the reduction of the 'matrix toxicity' was also observed.

---

* Corresponding author, ✉ jiri.palarcik@upce.cz

Introduction

Pharmaceutical residues are ubiquitous environmental micropollutants. Although their concentrations are usually quite low, their chronic effects are considerable. In addition, existing wastewater treatment technologies are not designed to handle this specific class of pollutants, and their inadequate removal is commonly observed.

Diclofenac (DCL) is a nonsteroidal anti-inflammatory drug (NSAID) commonly used as an analgesic, anti-arthritic, and anti-rheumatic agent. The global consumption of DCL is estimated at nearly 1000 tons per year [1]. Some DCL is not completely metabolized after consumption, thus polluting wastewater treatment plants. The traces of DCL has been detected in municipal wastewater effluent, surface water, and groundwater at concentrations in the order from ng L^{-1} to µg L^{-1} (10^{-6} to 10^{-3} µM). Although DCL at these environmentally typical concentrations cannot cause lethal effects on organisms, chronic toxicity is potentially possible [2]. Due to these facts, DCL as a first pharmaceutical from NSAIDs, was included in the list of monitored substances in waterways, as stated in the 2013/39/EU Directive [3].

Recently, various methods for water purification have been developed, including chemical, electrochemical, photochemical, and membrane processes. Among these, processes using UV radiation have shown great potential in the treatment of pharmaceutical residues. Overall feasibility is dependent not only on the chemical properties of the substance, but also on the UV light source and, eventually, on the catalyst used. In the case of DCL, both direct and indirect photolysis can take place [4]. The degradation of DCL by heterogeneous photocatalysis with conventional UV light sources has already been reported by many authors [5]. A lot of excellent work on the reaction mechanism [6], the toxicity of intermediates [7], and novel catalysts [8] has been completed. However, description of specific phenomena that may arise when using UV-A LEDs as a UV source is still scarce.

Total mineralization of organic pollutants to CO_2, H_2O and inorganic salts is favorable in water treatment processes. Nevertheless, DCL may break into intermediate substances with different properties. There is evidence that some of the DCL degradation intermediates are significantly more toxic for non-target organisms than the DCL itself. Schmitt-Jansen et al. measured a six-fold enhanced toxicity in an algal test after 3.5 h of exposure of DCL to sunlight [9]. Calza et al. used a 1500 W Xe lamp as a UV source and TiO_2 P25 (Degussa) as a catalyst in photocatalytic experiments [10]. Toxicity to *Vibrio fischeri* increased rapidly from 24 % to 72 % just after 20 min, and then toxicity started to decrease. Increased toxicity was also registered using TiO_2 P25 (Degussa) and a 125 W fluorescent lamp emitting light between 300 and 420 nm in wavelength [11]. Photocatalytic irradiation of 40 mg L^{-1} of DCL toxicity to *Daphnia magna* was considerably greater in comparison to an untreated DCL solution after 120 min.

The light source is a vital factor because it imposes significant impact, not only on the operational and maintenance costs of the degradation system, but also on the complicated reaction schemes of the photocatalytic reactions. UV-based technologies have commonly used conventional mercury lamps, which have several important drawbacks, such as long-term exposure instability, low photonic efficiency, short lifetime, fragility, mercury toxicity, and ozone production. Recently, light emitting diodes (LEDs) have appeared as a new source of UV light in environmental heterogeneous photocatalytic systems. UV-LEDs are characterized by optical stability, low energy consumption, a lower emission of waste heat, a long lifetime, and a short warm-up time; thus, the possibility of periodic irradiation, and the absence of hazardous materials. At present, the limitation of the UV-LED sources is linked to a relatively low power emitted by each individual lamp and by the fact that the main emission of the UV-LED lamps occurs at about 360 nm; i.e. in the UV-A spectral range, which seems to be photochemically less useful than the emission in the UV-B and UV-C spectral ranges. Until now, only very few attempts have been made to use UV-A LEDs for the degradation of pharmaceuticals, namely, two antibiotics (sulfamethoxazole and oxytetracycline), as well as an endocrine disruptor hormone 17-α-ethynyl estradiol [12].

Therefore, the present study aims to define the efficiency of photolysis and TiO_2-mediated photocatalysis with a novel highly efficient UV-A LED irradiation source for the degradation of DCL in various water matrices. DCL was spiked at a level which is environmentally closer to more relevant drug residue concentrations. Degradation experiments were conducted in a batch photoreactor, which allowed us the evaluation of the effect of various operational parameters. In addition, to this date, there is no evidence of the influence of the UV-A LED source on the ecotoxicity of DCL degradation products. To determine the level of toxicity of the DCL intermediate products, the growth inhibition test with *Parachlorella kessleri* alga was used.

Materials and methods
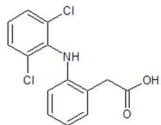
Chemicals and wastewaters

Three commercial nano- and micro-sized titania-based catalysts were tested: Degussa P25 (Evonik Industries, Essen, Germany), Hombikat UV 100 (Sachtleben Chemie, Duisburg; Germany), and AV-01 (Precheza, Přerov; Czech Republic). The properties of the catalysts, including particle size, isoelectric point (IEP) and specific surface area, are summarized in Table 1, indicating also the secondary particle size; i.e., the size of agglomerates determined by light scattering. Concentrated water dispersion of the catalyst particles was prepared by sonication of aqueous slurry of titanium dioxide for 30 min.

Table 1 Characteristics of the catalysts tested

Catalyst	Mean particle size [nm]	IEP	BET surface area [$m^2 g^{-1}$]	External surface area [$m^2 g^{-1}$]	Supplier
UV100	612	4.0	348	2.28	Sachtleben Chemie
P25	3527	6.7	56	0.40	Evonik Industries
AV-01	593	3.9	11	2.35	Precheza

DCL was supplied as a sodium salt at 99.5% purity (Sigma Aldrich, Prague, Czech Republic); its chemical and physical features being listed in Table 2. The feed solutions were prepared by the addition of 500 µg L^{-1} of the drug to the treated water. An additional concentration of 20 µg L^{-1} was used for algal tests.

Table 2 Chemical and physical properties of diclofenac

Parameter	DCL
Molecular formula	$C_{14}H_{11}Cl_2NO_2$
Structure	
Molecular weight [g mol^{-1}]	296.1
Log K_{OW}	4.4
Solubility in water [mg L^{-1}]	2.4
pK_a	4.15
UV absorption maximum [nm]	273

NaOH and/or HCl (Penta, Chrudim; Czech Republic) were used for pH adjustment. The concentration of H$_2$O$_2$ (30% stock solution, Lach-Ner, Neratovice; Czech Republic) used in the photocatalytic reactions was 0.5 g L^{-1}. Deionized water (with a conductivity of 4 µS cm^{-1}) was produced using the reverse-osmosis water purification system installed at University of Pardubice. The tap water was collected from the municipal water main of Pardubice City. Surface water was taken from the Elbe river in the central part of Pardubice (it has a relatively calm water flow rate of about 60 m^3 s^{-1}) during March 2016. The samples of wastewater were obtained from primary effluent (after mechanical treatment) of the municipal waste water treatment plant in Pardubice, which processes approximately 300 L of sewage waters per second.

The wastewater samples were diluted in a 1:1 ratio with deionized water and stored at 4 °C prior to use in the experiments. The water quality parameters, i.e. pH value, total organic carbon content (TOC), chemical and biochemical oxygen demand (COD_{Cr}, BOD_5) and conductivity, are surveyed in Table 3. Specifically, COD_{Cr}, TOC and light absorption at 254 nm (A_{254}) constitute a significant indication of the organic matter present in the matrices.

Table 3 Typical water quality parameters of matrices studied

Parameter	Tap water (TW)	Surface water (SW)	Wastewater (WW) [a]
pH	7.65	6.9	7.6
Conductivity [$\mu S\ cm^{-1}$]	670	330	720
COD_{Cr} [$mg\ L^{-1}$]	1.54	16	351
BOD_5 [$mg\ L^{-1}$]	–	5.7	68
TOC [$mg\ L^{-1}$]	0.2	6.3	115
A_{254} [–]	0.002	0.115	0.922

[a] After dilution

Experimental systems

The experiments were conducted in a batch 4L glass reactor equipped with a UV irradiation unit, a tempering system, and a powerful stirrer. A pitched blade impeller (with 6 blades) was used; the vessel to impeller diameter ratio was 4, and the optimum stirrer rotation was determined by the procedure described by Kertesz et al. to be 600 rpm [13]. The UV-A LEDs used for the study had a high-power mosaic array UV chipsets consisting of 12 UV LEDs (model CBM-120) from Luminus Devices (Sunnyvale, CA, USA), having a peak wavelength of 368 nm with a spectrum half-width of 5 nm, irradiance angle of 120 degrees, and a radiometric flux at a peak wavelength of 8.5 W. For the evaluation of radiation emitted by UV-LEDs and transferred into the reactor, ferrioxalate actinometry was also used [14]. The incident photon flux was determined as $9.42 \cdot 10^{-6}$ Es L^{-1} s^{-1}, i.e. 4.44 W L^{-1}.

In a typical run, the aqueous matrix containing the drug at an initial concentration of 500 μg L^{-1} was mixed with the appropriate amount of catalyst concentrate and stirred for 30 min in the dark to equilibrate the system. Then, the UV light was switched on to start the degradation process. In the case of heterogeneous photocatalysis, the samples were also centrifuged using a 5804R centrifuge (Eppendorf AG, Hamburg, Germany) to remove particles of the catalyst before analysis. The differences between the duplicate measurements were less than 10 %.

For comparison purposes, additional experiments without UV (adsorption), without TiO$_2$ addition (photolysis) and with the addition of H$_2$O$_2$ were also performed. Multiple measurements were carried out under identical reaction conditions to confirm the reproducibility.

Analytical procedures and sampling

The HPLC analysis was performed using a DeltaChrom 1000 LC chromatograph (Watrex, Prague, Czech Republic) with a photodiode array detection. As a stationary phase, a Nucleosil C18 analytical column was used. The mobile phase used a mixture of acetonitrile and acidified water (by H$_3$PO$_4$) in the ratio of 3:2. Isocratic flow was 1 mL min^{-1} and retention time of the DCL (measured at 273 nm) was 6 min. The samples were preconcentrated using 6 mg Oasis HLB columns (Waters, Milford, MA, USA) and a preconcentrating unit (Macherey-Nagel, Düren; Germany). For conditioning, organic solvent (methanol), deionized water and acidified deionized water (pH 4) were used. After sample addition, the drug was washed out with a mixture of 1:1 methanol/acetonitrile. Then, the volume was gently concentrated to 3 mL at 50 °C and reconstituted with deionized water.

COD$_{Cr}$ and BOD$_5$ were determined by LCI 500 and LCK 555 (Hach, Loveland, CO, USA) cuvette methods. TOC was measured using a Formacs TOC/TN analyzer (Skalar, Breda, The Netherlands). A particle-size distribution and zeta-potential of the TiO$_2$ catalysts were measured using a Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK). The morphologies of the TiO$_2$ powders were also examined using a 5600LV scanning electron microscope (JEOL, Tokyo, Japan).

Growth inhibition of *P. kessleri*

Algal cultures of the unicellular *P. kessleri* were cultured in solution according to OECD [15]. The initial cell concentrations were determined using an Eclipse 80i microscope with a Bürker chamber and DSFI-1 digital camera (Nikon, Kanagawa Japan) as $1\cdot10^5$ cells mL^{-1}. The cell growth inhibition was calculated by comparison of the total chlorophyll content with the average growth of unexposed control cultures. Total chlorophyll content was evaluated from the values of absorbance measured using a DR6000 spectrophotometer (Hach) at wavelengths of 632 nm, 652 nm, 665 nm, and 696 nm [16]. The average specific growth rate μ_{i-j} [day^{-1}] was calculated according to the equation (1):

$$\mu_{i-j} = \frac{\ln X_j - \ln X_i}{t_j - t_i} \qquad (1)$$

where t is time and X is chlorophyll content (in $\mu g\ mL^{-1}$) at time i or j. The inhibition of the growth rate I_r (in %) was calculated as:

$$I_r = \frac{\mu_c - \mu_t}{\mu_c} \qquad (2)$$

where index c is related to the control sample and index t to the treated sample.

Results and Discussion

Effect of UV photolysis

When studying photocatalysis, it is very important to separate the influence of photolysis, since it is expected to compete with the degradation of the substances induced by the action of the catalyst. For this purpose, a series of experiments was conducted with UV illumination without a catalyst in order to highlight DCL's ability of absorbing the radiation reaching the model system. Fig. 1 shows the typical results obtained after applying UV-A LED irradiation to the tap water matrix spiked by DCL.
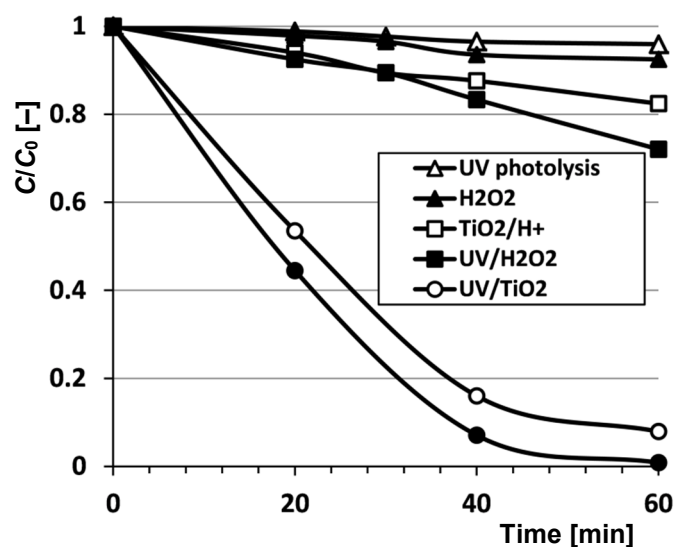

Fig. 1 Typical time dependencies of DCL concentration, C, during UV photolysis and photocatalysis, both with and without hydrogen peroxide addition

(tap water matrix; initial drug concentration $C_0 = 500\ \mu g\ L^{-1}$; catalyst 0.5 g L^{-1} of AV-01; H_2O_2 0.5 g L^{-1})

As observed, the drug was only slightly photodegraded by direct UV photolysis: only 4.1 % of DCL was removed in 60 min. Moreover, it was also found that direct photolysis was not able to mineralize the drug under the experimental

conditions used; the values of TOC and COD_{Cr} remaining unchanged during the experiment (not depicted in Fig. 1). This behavior can be explained because the DCL absorption maximum (see Table 2) does not overlap the spectra of the incoming radiation simulated by the UV-A LED lamp with narrow peak emission in the range 363–373 nm. Thus, the irradiation is poorly absorbed by the drug and cannot thus contribute to the generation of electronically-excited states, which is needed as the first step of the reaction mechanism in direct photolysis [17].

Some studies have reported on an increased removal efficiency of DCL using a combination of UV and hydrogen peroxide. In this case, the process of H_2O_2 decomposition takes place, which can be generally described by a simple reaction scheme [18]:

$$H_2O_2 + h\nu \rightarrow [2 \bullet OH] \tag{3}$$

The hydroxyl radicals formed are very strong oxidizing agents and can easily attack the drug molecules, thus leading eventually to their complete mineralization. The dosing of hydrogen peroxide was tested in the concentration range of 0.1 g L^{-1} to 2 g L^{-1}; the best results being obtained at 0.5 g L^{-1} of H_2O_2. However, as can be seen in Fig. 1, photolysis combined with the addition of hydrogen peroxide still shows a slow progression in the DCL removal. The degradation of DCL was incomplete, reaching only 27.9 % within the chosen time frame. This was expected, as H_2O_2 absorbance compared to DCL extends slightly to the UV-A LED source spectrum; nevertheless, the H_2O_2 absorbs UV radiation of wavelength <380 nm [19]. This agrees with the experimental results of Cataldo [20], who found the UV-A LED photolysis of hydrogen peroxide weak, with the rate constant two orders of magnitude lower than that achieved with traditional mercury arc lamps.

Effect of adsorption

The variation in adsorption of DCL onto TiO_2 was studied at a typical pH of 6.7 and an acidic pH of 3. The experiments were performed in the dark using aqueous suspensions containing 0.5 and 5 g L^{-1} of TiO_2. The suspensions were continuously stirred at a constant temperature with a magnetic bar for 1 h. The adsorption capacity (as μg of substance per g of catalyst), was calculated from the difference in drug concentration in the aqueous phase before and after adsorption.

Generally, adsorption can play an important role, because degradation of organic substances preferably takes place during the adsorbed phase on the surface of the catalyst [21]. For the systems studied, the catalyst adsorption capacity was very low and the changes in concentration were undetectable with the analytical method's level of accuracy. To increase the amount of the drug removed, the catalyst concentration was increased to 5 g L^{-1} in the adsorption

experiments. Then, the highest adsorption capacity for a portion of 145 µg g^{-1} was obtained at pH 3, whereas the adsorption capacity at the typical pH was 48 µg g^{-1}. The increase in the adsorption of DCL with decreasing pH can be explained by considering the surface charge of both the adsorbent material and the substrate. The TiO$_2$ surface is positively charged in acid media, whereas it is negatively charged under neutral and alkaline conditions (see IEP in Table 1). Also, DCL can be dissociated at acidic pH, since the pKa value is close to 4 (see Table 2). Thus, the most intensive adsorption was observed at pH 3, because the positive charges at the surface of the catalyst had attracted the DCL anions. For example, complete DCL removal was reached at pH 3 after 1 hour of irradiation, whereas in alkaline conditions (at pH 12) the removal was less effective attaining only 50.5 % under the same conditions. This behavior can be attributed to the repulsion between the surface of the TiO$_2$ and the DCL molecule.

Effect of catalyst

It is well documented that irradiation of an aqueous TiO$_2$ suspension with light energy that is greater than the band gap energy of the semiconductor (e.g. >3.2 eV for anatase) needed to carry out the degradation photocatalytic process; i.e. UV irradiation with a wavelength of lower than 380 nm [15]. A UV-A LED source using a precisely-determined narrow wavelength range close to the upper process limit is therefore appropriate for testing photocatalytic efficiency with various catalysts.
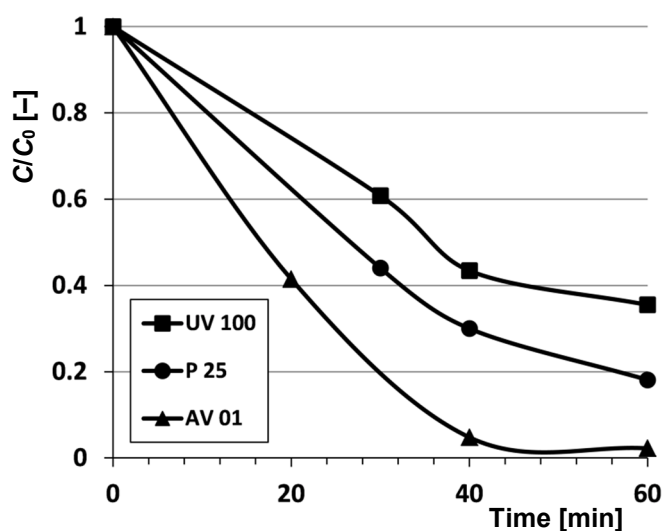

Fig. 2 Typical time dependencies of DCL concentration, *C*, during photocatalysis with various TiO$_2$ photocatalysts

(tap water matrix; initial drug concentration C_0 = 500 µg L^{-1}; catalyst concentration 0.5 g L^{-1})

Dosing of the TiO_2 catalyst was tested in the concentration range of 0.25 to 2 g L^{-1} and the best results were obtained at a concentration of 0.5 g L^{-1} of TiO_2 for all catalysts tested. The experimental results (see Fig. 2) show that DCL removal with AV-01 catalyst showed good performance; indeed, after just 1 hour, the DCL removal was about 90 % (see also Fig. 2). After 2 hours, the drug was totally degraded and decomposed. The P25 catalyst showed lower photodegradation rates, which after 1 hour reached 81.9 % for DCL. For the UV100 catalyst, degradation was 64.5 %.

In general, the particle size is an important parameter for catalysis since it directly impacts the specific surface area of a catalyst. With a smaller particle size, the number of active sites increases, as does the surface charge carrier transfer rate in photocatalysis [22]. However, our experimental results have shown that the apparent particle size can change significantly in TiO_2-mediated photocatalysis because of the particle aggregation. For example, it is generally accepted that the primary size of P25 catalyst particles is 21 nm [23], while our light scattering measurements using Malvern Zetasizer have revealed a secondary value of approximately 170× larger (see again Table 1). Thus, the secondary external surface area, a, that is involved in 1 g of aggregated TiO_2 catalysts when the particles are regarded as spherical, was calculated from the secondary mean particle diameter, d, as:

$$a = \frac{6}{1000\, d\, \rho} \tag{4}$$

where ρ is density of TiO_2 (4230 kg m^{-3}).

The respective results are given in Table 1. As seen, the AV-01 and Hombikat UV100 catalysts have nearly the same secondary external surface areas, whereas Aeroxide P25 is more easily aggregated under the given conditions (the pH value is closer to the IEP point) and generates larger clumps with a smaller external surface area. Here, it is necessary to note that no direct correlation between the catalyst activity and the catalyst BET surface area was found. It is probable that true accessibility of the inner active centers of catalyst for both the large drug molecules and UV light is limited for the aggregated highly-nanostructured materials used. Of course, the catalyst activity may also be affected by active site density and other structural parameters that result from the catalyst preparation procedure. All the mechanisms described appear to play specific roles in these complicated multicomponent systems resulting, for example, in the best drug degradation with Precheza AV-01 microstructured photocatalyst. In view of these results, all the subsequent runs were conducted with Precheza AV-01 catalyst.

Effect of matrices

The data reflecting the influence of tested matrices on the removal of DCL during heterogeneous photocatalysis are summarized in Table 4 and typical time dependences for DCL degradation shown in Fig. 3. Certain removals of DCL were detected in all three types of water matrix. In general, in the tap-water matrix, the efficiency of removal of DCL was 92 %. The degradation of DCL in both the surface and wastewater matrix showed lower efficiencies. In the surface water matrix, the concentration of DCL was reduced by 83 %, and only 12 % for DCL in the wastewater matrix. From the experimental data, it is also evident that the percentages of COD_{Cr}, BOD_5 and TOC removal are almost the same in surface and wastewaters. Only in the case of BOD in tap water, the value is increased due to the higher biodegradability of the DCL intermediates generated. According to Calza et al., DCL disintegration is mainly associated with the breakup of the C–N bond and chlorine cleavage into chloride ions [10]. These findings agree with Rioja et al., where the order of DCL degradation has been as follows: deionized > tap > river > wastewaters [24]. After 0.5 mg L^{-1} H_2O_2 addition to the photocatalytic system, DCL degradation increased substantially in both surface and wastewater matrices. In the surface water matrix, the removal of DCL was 90 %. In the wastewater matrix, it went down to 70 %.

Table 4 Ratios of various process parameters after 1 hour of heterogeneous photocatalysis for the matrices tested

Parameter	Type of matrix		
	Tap water (TW)	Surface water (SW)	Wastewater (WW)
C/C_0	0.08	0.170	0.714
$COD/(COD)_0$	0.857	0.670	0.715
$BOD/(BOD)_0$	3.0	0.801	0.619
$TOC/(TOC)_0$	0.90	0.841	0.772
$A_{254}/(A_{254})_0$	0.20	0.872	0.617
k [min^{-1}]	0.043	0.033	0.003
$t_{1/2}$ [min]	16.31	21.20	277.3

During photocatalytic experiments, pseudo-first order reaction kinetics were confirmed as can be seen from the typical linear dependences in Fig. 3. The reaction rate constant, k, was obtained by linear regression, as depicted by the slope of dependencies. Coefficients of determination (R^2) varied from 0.965 to 0.991. The results are shown in Table 4. It can be seen that the rate constants in

tap water and surface water are comparable. Nevertheless, the rate constant value is one order lower in the case of waste water. After the addition of hydrogen peroxide into the reaction mixture, the rate constants increased in all types of matrices. The best results were obtained for the tap water matrix, where the rate constant was $7.1 \cdot 10^{-2}$ min^{-1}. Reasonable results were also for the wastewater matrix, where the rate constant increased significantly to $2.1 \cdot 10^{-2}$ min^{-1}.

According to the half-life of the drug molecule, $t_{1/2}$, is calculated as:

$$t_{1/2} = \frac{\ln 2}{k} \qquad (5)$$

To eliminate half an amount of DCL in the surface water, 21 minutes are necessary. But in wastewater, 4.6 hours is needed for the same degradation of DCL. However, after addition of hydrogen peroxide, the half-live of DCL in wastewater decreased significantly when a value of 34 min was obtained. According to these findings, the removal rate of DCL in real matrices is more dependent on the aqueous matrix, in which the DCL is contained, than on the chemical structure of this micropollutant. The effluent organic constituents can hinder the photocatalytic treatment of DCL in two ways: (1) by providing a substantial quantity of organic moieties to the scavenged photogenerated •OH; and (2) by adsorbing onto the TiO$_2$, which reduces the availability of surface active sites for the target substrate and the subsequent oxidation with surface-bound •OH.
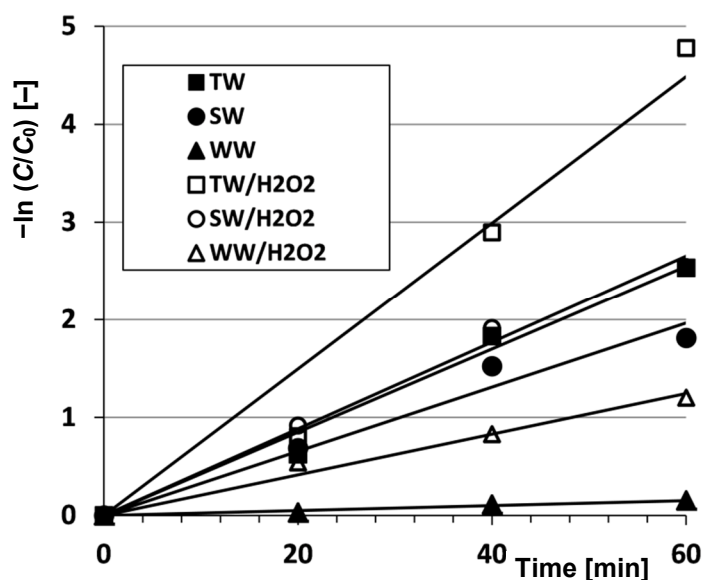

Fig. 3 Reaction rate constants determination during the heterogeneous photocatalysis in different types of matrices with and without hydrogen peroxide addition

(0.5 g L^{-1} of AV 01; H$_2$O$_2$ 0.5 g L^{-1})

Ecotoxicity of diclofenac and its intermediates with respect to *P. kessleri*

As can be seen from Table 4, total DCL mineralization was not achieved in all sets of experiments. Therefore, the toxicity of water samples containing residues of DCL and its phototransformation intermediates was assessed by changes in the total chlorophyll content of *P. kessleri*. The results shown in Fig. 4 indicate that the phytotoxicity decreased after UV-A LED photocatalytic degradation. For example, in the case of DCL spiked in waste and surface water, the overall toxicity of the mixture decreased almost by 80 %. The significant toxic effect caused by the water matrix itself was also detected.
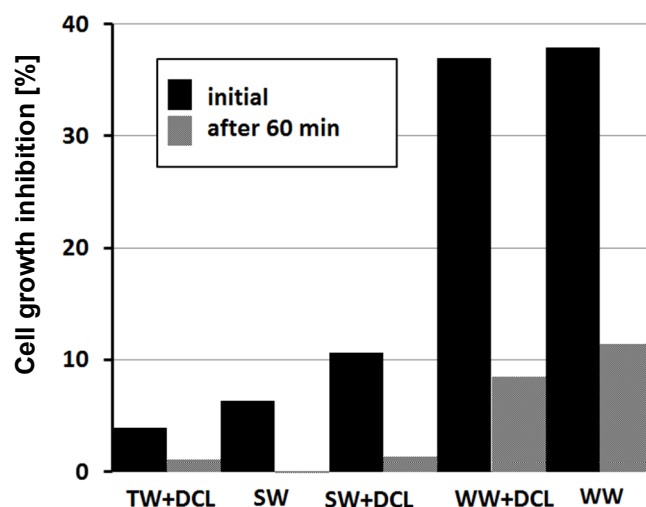

Fig. 4 Cell growth inhibition of *P. kessleri* – initial and after 60 min of UV-A photocatalytic degradation

(waters were spiked with 500 μg L^{-1} of DCL; 0.5 g L^{-1} of AV 01)

Although promising results were achieved, the described method was insufficiently sensitive to differentiate the DCL contribution to the total cell growth inhibition. To obtain better evidence of DCL behavior during heterogeneous photocatalysis, a DCL concentration of 20 mg L^{-1} was used in further measurements of toxicity. As seen from Fig. 5, a higher initial amount of DCL caused a relatively high toxic effect on *P. kessleri*, giving an algal growth inhibition of 62 %. This is comparable with the results obtained by Rizzo et al. [11]. On the other hand, when UV-A LED photolysis had started, toxicity decreased indicating the formation of a less toxic product. Despite the relatively short time schedule of the experiments, phytotoxicity decreased by 45 % during one hour of irradiation.
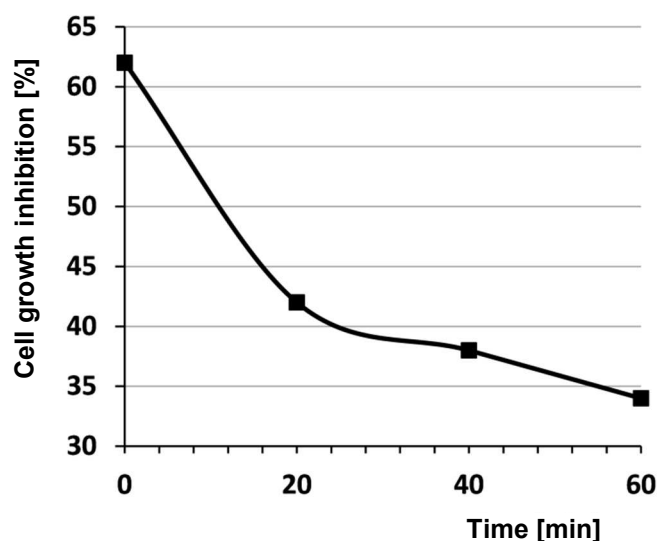
Fig. 5 Dependence of cell growth inhibition of P. *kessleri* on time during photocatalytic irradiation of DCL solution

(20 mg L^{-1} of DCL in tap water; 0.5 g L^{-1} of AV 01)

Conclusions

In this study, the results have demonstrated that UV-A LED represents a practical and competitively alternative light source for photocatalytic destruction of the DCL residues contained in various aqueous systems. The degradation tests were significantly influenced by several factors, such as the zeta potential of catalyst particles, the absorption spectral overlap between the drug and UV source, the electrostatic interaction (attractive or repulsive), and, finally, the properties of drug degradation intermediates.

The experimental results indicated that a UV-A LED source operating at a wavelength of 368 nm had a much better efficiency in combination with Precheza AV-01 microstructured anatase type photocatalyst than that of standard Degussa P25 catalyst. For the systems studied, the catalyst adsorption capacity for DCL was found very low; however, at acidic pH, the adsorption capacity increased because the positive charge on the surface of the catalyst attracted the DCL anions. Equally, direct UV-A photolysis had a minor effect on DCL removal, indicating that within the narrow region of emission spectra, the UV-A LED source is capable of removing DCL only when being coupled with a TiO_2 catalyst. Even in the case of the addition of hydrogen peroxide to the reaction mixture, the removal only increased to 30 % during UV photolysis. The photocatalytic effect of UV-A LED/TiO_2 was significant in all water matrices, but the removal rate of diclofenac from the wastewater matrix was more dependent on the matrix itself than that based on the chemical structure of the micropollutant. The addition of

hydrogen peroxide to the photocatalytic system enhanced the removal rates. Although DCL removal was relatively high, the complete mineralization did not occur. The results of the algal growth inhibition test then revealed a significant reduction of toxicity to *P. kessleri* after UV-A LED irradiation of the diclofenac solution. In addition, the reduction of the "matrix toxicity" was also observed.

Acknowledgments

References

[1]   Chen B.J., Gao H.W., Zhang Y.L., Zhang Y., Zhou X.F., Li C.Q., Gao H.P.: Developmental toxicity of diclofenac and elucidation of gene regulation in zebrafish (*Danio rerio*). *Scientific Reports* **4** (2014) 1–7.

[2]   Brown J.N., Paxeus N., Förlin L., Larsson D.G.: Variations in bioconcentration of human pharmaceuticals from sewage effluents into fish blood plasma. *Environmental Toxicology and Pharmacology* **24** (2007) 267–274.

[3]   Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy (Text with EEA relevance). http://data.europa.eu/eli/dir/2013/39/oj (accessed: June 1, 2019).

[4]   Packer J.L., Werner J.J., Latch D.E., McNeill K., Arnold W.A.: Photochemical fate of pharmaceuticals in the environment: naproxen, diclofenac, clofibric acid, and ibuprofen. *Aquatic Sciences* **65** (2003) 342–351.

[5]   Plakas K.V., Sarasidis V.C., Patsios S.I., Lambropoulou D.A., Karabelas A.J.: Novel pilot scale continuous photocatalytic membrane reactor for removal of organic micropollutants from water. *Chemical Engineering Journal* **304** (2016) 335–343.

[6]   Martínez C., Canle M.L., Fernández M.I., Santaballa J.A., Faria J.: Aqueous degradation of diclofenac by heterogeneous photocatalysis using nanostructured materials. *Applied Catalysis B* **107** (2011) 110–118.

[7]   Aguinaco A., Beltrán F.J., García-Araya J.F., Oropesa A.: Photocatalytic ozonation to remove the pharmaceutical diclofenac from water: influence of variables. *Chemical Engineering Journal* **189**–**190** (2012) 275–282.

[8]   Das L., Barodia S.K., Sengupta S., Basu J.K.: Aqueous degradation kinetics of pharmaceutical drug diclofenac by photocatalysis using nanostructured titania–zirconia composite catalyst. *International Journal of Environmental Science and Technology* **12** (2015) 317–326.

[9]   Schmitt-Jansen M., Bartels P., Adler N., Altenburger R.: Phytotoxicity assessment of diclofenac and its phototransformation products. *Analytical and Bioanalytical Chemistry* **387** (2007) 1389–1396.

[10]   Calza P., Sakkas V.A., Medana C., Baiocchi C., Dimou A., Pelizzetti E., Albanis T.: Photocatalytic degradation study of diclofenac over aqueous TiO_2 suspensions. *Applied Catalysis B* **67** (2006) 197–205.

[11]   Rizzo L., Meric S., Kassinos D., Guida M., Russo F., Belgiorno V.: Degradation of diclofenac by TiO_2 photocatalysis: UV absorbance kinetics and process evaluation through a set of toxicity bioassays. *Water Research* **43** (2009) 979–988.

[12]   Malkhasian A.Y.S., Izadifard M., Achari G., Langford C.H.: Photocatalytic degradation of agricultural antibiotics using a UV-LED light source. *Journal of Environmental Science and Health, Part B* **49** (2014) 35–40.

[13]   Kertesz S., Cakl J., Jiránková H.: Submerged hollow fiber microfiltration as a part of hybrid photocatalytic process for dye wastewater treatment. *Desalination* **343** (2014) 106–112.

[14]   Hatchard C.G., Parker C.A.: A new sensitive chemical actinometer – II. Potassium ferrioxalate as a standard chemical actinometer. *Proceedings of the Royal Society of London A* **235** (1956) 518–536.

[15]   OECD Test No. 201: *Freshwater Alga and Cyanobacteria, growth inhibition test*. OECD Publishing, Paris 2011.

[16]   Ritchie R.J.: Consistent sets of spectrophotometric chlorophyll equations for acetone, methanol and ethanol solvents. *Photosynthesis Research* **89** (2006) 27–41.

[17]   Oppenländer T.: *Photochemical purification of water and air advanced oxidation processes (AOPs): Principles, reaction mechanisms, reactor concepts*. Wiley-VCH, New York 2003.

[18]   Rivas J., Gimeno O., Boralho T., Beltrán F.: Influence of oxygen and free radical's promoters on the UV-254 nm photolysis of diclofenac. *Chemical Engineering Journal* **163** (2010) 35–40.

[19]   Luňák S., Sedlák P.: Photoinitiated reactions of hydrogen peroxide in the liquid phase. *Journal of Photochemistry and Photobiology A* **68** (1992) 1–33.

[20]   Cataldo F.: Hydrogen peroxide photolysis with different UV light sources including a new UV-LED light source. *New Frontiers in Chemistry* **23** (2014) 99–110.

[21]   Herrmann J.M.: Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today* **53** (1999) 115–129.

[22]   Zhang Z., Wang C., Zakaria R., Ying Y.J.: Role of particle size in nanocrystalline TiO_2-based photocatalysts. *Journal of Physical Chemistry B* **102** (1998) 10871–10878.

[23]   Imani R., Pazoki M., Iglič A.: TiO_2 nanostructured materials: Synthesis and applications, in: Aliofkhazraei M. (Ed): *Handbook of functional nanomaterials*, Nova Science Publishers, New York 2014, pp. 309–335.

[24]   Rioja N., Benguria P., Penas F.J., Zorita S.: Competitive removal of pharmaceuticals from environmental waters by adsorption and photocatalytic degradation. *Environmental Science and Pollution Research* **21** (2014) 11168–11177.