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**Diclofenac and Naproxen Removal from Aqueous
Matrices by Heterogeneous Photocatalysis**

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Abstract

This study investigated the issue of diclofenac and naproxen residues in the environment, specifically the application of heterogeneous photocatalysis for removal of such drug residues from various water matrices. The theoretical part describes the effect of the pharmaceuticals on aquatic ecosystems, the methods of drug residues analysis, and the techniques of their removal. The analytical SPE-HPLC method was optimized for the determination of extremely low drug concentrations in complicated matrices. Photocatalytic drug degradation was studied using a laboratory-scale photoreactor equipped with UV-A LED diodes, with maximum emission spectrum at 365 nm. The experimental results showed that the efficiency of the process depended on the type and the concentration of both the catalyst and substrate as well as on the operating conditions of the UV-A LED source. There was a significant relationship between the water matrix composition and the effectiveness of the TiO₂ photocatalytic process, with lower reaction rates with the pharmaceuticals dissolved in surface and wastewaters due to the organic matter present which consume some of the oxidant agents. The pH of the water matrix to which pharmaceuticals were added significantly affected the degradation, since it dictates the charge of catalyst particles, consequently the adsorption of substrates onto the catalyst surface. The presence of H₂O₂ in the reaction mixture enhanced the oxidation rates, with the UV/TiO₂/H⁺/H₂O₂ system providing the highest efficiency. The by-products did not show a higher toxic effect on *Parachlorella kessleri* algae than the original drugs.

Abstrakt

Disertační práce se zabývá problematikou reziduí léčiv diklofenaku a naproxenu v životním prostředí, konkrétněji uplatněním heterogenní fotokatalýzy v rámci odstraňování těchto léčiv z různých vodných matric. Teoretická část popisuje vliv léčiv na vodní ekosystémy, metody analýzy reziduí léčiv a techniky jejich odstraňování. V experimentální části byla nejprve optimalizována analytická SPE-HPLC metoda pro stanovení extrémně nízkých koncentrací léčiv ve složitých matricích. Fotokatalytická degradace léčiva byla studována v laboratorním fotoreaktoru vybaveném UV-A LED diodami s maximální emisí při 365 nm. Experimentální výsledky ukázaly, že účinnost procesu závisí jak na typu a koncentraci katalyzátoru a substrátu, tak i na inženýrských procesních charakteristikách fotokatalýzy. Byl zejména pozorován významný vztah mezi složením matrice a účinností fotokatalytického procesu. Nižší reakční rychlosti byly získány s farmaceutiky rozpuštěnými v povrchové a odpadní vodě, zejména v důsledku přítomnosti řady organických látek, které spotřebovávají významné množství oxidačních činidel. Degradaci léčiv významně ovlivňovala i hodnota pH matrice, do které byla přidávána léčiva, protože předurčuje náboj částic katalyzátoru a následně adsorpci substrátů na povrchu katalyzátoru. Přítomnost H₂O₂ v reakční směsi zvýšila rychlost degradace, přičemž systém UV/TiO₂/H⁺/H₂O₂ vykazoval nejvyšší účinnost. Rozkladné produkty nevykazovaly vyšší toxický účinek na sladkovodní řasu *Parachlorella kessleri* než původní léčiva.

Keywords:

Pharmaceuticals, Diclofenac, Naproxen, Heterogeneous Photocatalysis, Aqueous Matrices, LED diodes

Klíčová slova:

Léčiva, diklofenak, naproxen, heterogenní fotokatalýza, vodné matrice, LED diody

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1 Introduction

Pharmaceutical residues are ubiquitous environmental micropollutants, which are introduced into the environment in various ways. They are detected in wastewater worldwide, including the Czech Republic. Although their concentrations in the environment are relatively low, their chronic effects are considerable.

Diclofenac (DCL) and naproxen (NPR) are a non-steroidal anti-inflammatory drugs (NSAIDs) commonly used as an analgesic, anti-arthritic, and antirheumatic agents. However, they are not completely metabolized after consumption and are discharged to wastewater treatment plants (WWTPs). Currently, the elimination of DCL or NPR by conventional treatment processes is not sufficient, as they are not appropriate substrates for activated sludge bacteria, often causing inhibition of the sludge bacteria due to their high biological activity.

DCL and NPR have been detected in municipal wastewater effluent, surface water, and groundwater at concentrations in the order of ng/L to $\mu\text{g/L}$. Although these environmental concentrations could not cause lethal effects on organisms, chronic toxicity is potentially possible¹.

For the reasons mentioned above, it is necessary to develop new processes suitable for the removal of biologically non-degradable substances, such as residual pharmaceuticals. Such modern techniques include advanced oxidation processes, specifically heterogeneous photocatalysis.

1.1 Photocatalytic processes for water treatment

Heterogeneous photocatalysis is a process that uses generation of hydroxyl radical to destroy organic substances. Compared to other methods, this process is relatively non-selective, therefore it is suitable for a wide range of contaminants.

Heterogeneous photocatalysis is characterized by the formation of electron (e^-) and hole (h^+) after excitation of the catalyst, typically TiO_2 , by UV irradiation. In contrast to the classical catalytic reaction, the activity of the catalyst is initiated by photons. In some cases, e^- transfers to the surface of the catalyst and subsequent reduction of electron acceptor may occur, with O_2 being reduced to O_2^- superoxide radical. Similarly, h^+ migrates to the catalyst surface where the e^- donor is oxidized, for example, oxidation of an organic substance or H_2O to the hydroxyl radical HO^\cdot may occur. This radical is a very strong oxidant (2.8 V), which oxidizes most organic substances to carbon dioxide and water.

Heterogeneous photocatalysis is a process comprising a catalyst, light source and substrate. Among catalysts, the most commonly used is TiO_2 because of its thermal, chemical and physical stability, low environmental impact and low cost. Photocatalytic activity is influenced by several factors such as crystal structure, particle size and porosity.

Photocatalytic process is also influenced by the source of irradiation. The radiation wavelength must be such that the catalyst electrons will obtain energy necessary to overcome the band gap. The band gap energy depends on the type of catalyst, for the

anatase TiO₂ catalyst, it is 3.2 eV, which equals the radiation wavelength of 387 nm and lower. To obtain the mentioned wavelength, UV lamps (mercury or xenon) emitting in the range of 250–400 nm are usually used. Recently, light emitting diodes (LEDs) have emerged as a new source of UV light in heterogeneous photocatalytic systems. UV-LEDs are characterized by optical stability, low energy consumption, lower emission of waste heat, a long lifetime, short warm-up time, thus the possibility of periodic irradiation, and the absence of hazardous materials as well as ozone production. Recently, the best UV-A sources emit radiation in the range of about 360 nm, which is less suitable for direct photolysis, but sufficient to be absorbed by anatase type TiO₂ catalysts.

The design of photoreactors depends on the form of the photocatalyst. If the photocatalyst is in suspension, the rate of the photocatalytic reaction is often faster compared to the immobilized form. The photocatalytic rate is also dependent on the amount of photocatalysts. Ideally, all the photocatalyst particles are irradiated and participate in the photocatalytic reaction. Above this optimum value, however, excessive photocatalyst prevents the penetration of photons to the surface of the individual catalyst particles. Similarly, at higher concentrations of the photocatalyst in the suspension, agglomeration of the particles occurs, so the specific surface area is reduced².

1.2 State of the art of use heterogeneous photocatalysis for diclofenac and naproxen removal

Typical experimental arrangements used for heterogeneous photocatalysis of NPR and DCL are shown in Table 1. It is clear that, with the exception of nanofibers, suspension reactors are used in different configurations with volumes ranging from 0.1 to 0.5 L, with the commercially available Aeroxide P-25 was used as a photocatalyst in a concentration range of hundreds of mg/L to units of g/L. Radiation was provided by lamps emitting in the UV-C or UV-B region, as well as solar radiation. The amount of pharmaceuticals in the studied systems was mostly in the order of mg/L due to the subsequent analytical assessment used for the determination of degradation by-products, which is why the drugs were prepared in deionized water (DI). In the case where the mechanism of photocatalytic decomposition was not studied, the drugs were irradiated in real matrices (municipal wastewater).

Reaction mechanisms of heterogeneous photocatalysis of DCL and NPR, that is, breakdown reaction intermediates, were mostly separated by high pressure liquid chromatography (HPLC) and identified by mass spectrophotometry. The DCL (NPR) degradation mechanism is dependent on the process conditions (type, quantity and properties of the photocatalyst, radiation source, etc.), so various intermediates with different physico-chemical properties may be formed, hence the toxic effect on non-target organisms may vary.

Table 1 Experimental studies of diclofenac and naproxen removal by heterogeneous photocatalysis

Catalyst (g/L)	UV source	Matrix	Reactor (volume, type)	NSAID (mg/L)	t_{exp} (h)	Degradation mechanism	Source
TiO ₂ Aeroxide 0.25	Sunlight	Municipal WW	5L flow	DCL 0.2	12	No	3
TiO ₂ 0.3	250 W	DI	5L flow	DCL 20	2	Intermediates	4
TiO ₂ Aeroxide 0.5	9 W, 350-400 nm	DI	Submersible	DCL 10	2	Yes	5
TiO ₂ nanofibers	Low pressure 264 a 365 nm	DI	0,1L	NPR 0.2	1	Intermediates	6
TiO ₂ Aeroxide 0.5-2.5	High pressure 323 nm	DI, municipal WW	1L tubular	DCL 0.5-80	2	No	7
TiO ₂ Aeroxide 0.5	24 W, 365 nm	DI	Flow	DCL 2	8	Intermediates	8

2 Aims of the Thesis

Despite the study of various aspects of heterogeneous photocatalysis process to remove DCL and NPR residues from wastewater, this issue requires further investigation, therefore this study aimed to:

- design a laboratory stirred batch reactor equipped with a UV-A LED radiation source, verify its functionality and identify optimal operating conditions for photocatalytic decomposition of DCL and NPR residues,
- describe and evaluate the specifics of the photocatalytic decomposition process of DCL and NPR during heterogeneous photocatalysis,
- determine the influence of selected matrices on the efficiency of DCL and NPR removal by heterogeneous photocatalysis, describe and evaluate the effect of real water composition on the efficacy of the removal of both drugs,
- verify the influence of pH and H₂O₂ on the process of heterogeneous photocatalysis of DCL (NPR) in real water matrices,
- design and validate a method for determination of DCL and NRP with regard to the detection of these drugs in aqueous solutions in the order of µg/L. Subsequently, verify this method within the analytical determination of drugs in surface and wastewater samples,
- determine and assess the toxic effect of DCL, NPR and possible products generated during photocatalytic drug degradation.

3 Experimental

3.1 Materials

DCL and NPR (in the form of sodium salts) were obtained from Sigma Aldrich. The solvents methanol (MeOH) and acetonitrile (ACN) were from Lach-Ner. Inorganic salts (mainly for algal medium) were analytical grade. Hydrochloric acid, phosphoric acid and sodium hydroxide were used to adjust the pH of the matrix or mobile phase in the chromatographic analysis. The purity of these chemicals was p. a. grade.

Samples of drinking water (DW), surface river water (SW) and wastewater (WW) were used as matrices for the study of individual photocatalytic processes. SW samples were collected in March 2016 from the river Labe in Pardubice into plastic samplers and immediately filtered using conventional pulp filter paper. Samples of WW were taken in March 2016 from an inlet of municipal WWTP in Pardubice-Rybitví. Due to the absence of solid particles in water there was no need to filtration and samples were stored in the dark at 4°C. DW and deionized water (DI) were taken from the water supply of the Institute of Environmental and Chemical Engineering of the University of Pardubice.

3.2 Experimental procedures

3.2.1 Solid phase extraction

The sorbent used was reverse-phase Oasis HLB, with 20 mL of MeOH, 6 mL DI and 6 mL of DI H₂O at pH 4 used for sorbent conditioning. During elution, the effect of MeOH, ACN or mixtures of both were investigated. The volume was concentrated to 3 mL at 55°C, then the effect of 2 mL of MeOH, ACN or mixtures of both with H₂O as reconstitution solvents were explored.

The precision and accuracy of the method was expressed by the relative standard deviation (RSD) and recovery (R) according to EPA guidance⁹.

3.2.2 Heterogeneous photocatalysis of pharmaceuticals

The experiments were conducted in a batch reactor with total volume of 5 L. A rotary stirrer with 6 blades (1 x 11.5 cm) was placed at the bottom of the cylinder and the reactor was covered by a plastic lid with round cutouts for UV source, aeration and measurement of additional parameters. As a UV-A radiation source, UV-A LED chip (Luminus) with twelve diodes was used, with an emission maximum of UV-A LED according to the data sheet at 365–370 nm.

Three commercially available photocatalysts were tested: Degussa (Aeroxide) P-25 (Evonik), Hombikat UV-100 (Sachtleben) and AV-01 (Precheza). Catalyst suspensions were prepared by mixing 2 g of the appropriate TiO₂ with 500 mL of DI, followed by

ultrasound homogenization for 30 min. Afterwards, the suspension was quantitatively transferred into the batch reactor.

The reactor was filled with 4 L of DW, SW or WW. An appropriate amount of the drug was dissolved to obtain the desired input concentration of 500 $\mu\text{g/L}$ or 20 mg/L . Optimal aeration with membrane blower and stirring was also evaluated. The pH varied from 3 to 12. Samples of the reaction mixture were taken at 20-minute intervals into 50 ml polypropylene tubes, centrifuged (12,000 rpm for 5 minutes) and the concentration of DCL (NPR) was determined by SPE-HPLC. The conversion of the individual drugs (X) was determined as a percentage loss of drug content in the sample relative to the initial drug concentration. The rate constant k was obtained by linear regression of the measured data. Determination coefficients (R^2) ranged from 0.97–0.99.

3.2.3 Toxicity of pharmaceuticals and its by-products

Due to the photolytic effect of UV radiation or the secondary effect of hydroxyl radicals, the breakdown of the parent molecule to a more toxic product may occur. The toxic effect of DCL (NPR) was evaluated as inhibition of *Parachlorella kessleri* algae growth after 72-hour exposure to the pharmaceuticals. Then, the algal suspension was filtered and chlorophyll was extracted using 5 mL of methanol in the dark place at 4°C. After extraction, the total amount of chlorophyll was quantified by UV/VIS spectrophotometry. Growth inhibition (%) was expressed as a difference in growth rates for algae exposed to the test substance versus control.

4 Results

4.1 Preconcentration by Solid phase extraction

MeOH, ACN and their mixtures were used as solvents to elute DCL (NPR) from the sorbent. A relatively high recovery in the range of 85–100% was achieved for all solvents used, with the highest yield obtained for the mixture of ACN with MeOH when 100% of the drug was eluted. The RSD ranged from 0.7–4.8% (see Table 2).

The next step was reconstitution after concentration of the sample. Table 3 shows solvent recovery and RSD after reconstitution by various solvents, with a relatively high yield in the range of 80–100% achieved. Reconstitution by MeOH generally showed lower yields in comparison to those reconstituted by ACN or H₂O, which may be associated with a better mixing of the sample with the MP, which also consists of a mixture of ACN and DI in a 3:2 ratio.

The modified solid phase preconcentration method was used to pretreat samples of 500 µg/L with each pharmaceutical spiked into SW and WW. From the analysis of the chromatograms, it was found that a high organic load (chemical oxygen demand COD_{Cr} 350 mg/L for WW) does not affect the amount of DCL (NPR) after extraction from the samples. Likewise, chromatographic analysis is unaffected because residual organic substances co-eluted with drugs were separated at different retention times.

Table 2 Recovery values of different solvents (in %) used for DCL (NPR) elution

Solvent	DCL				NPR			
	RSD _{UV/VIS} (%)	R (%)	RSD _{HPLC} (%)	R (%)	RSD _{UV/VIS} (%)	R (%)	RSD _{HPLC} (%)	R (%)
MeOH	4.5	97	4.7	97	2.6	85	3.3	100
ACN:MeOH	3.3	99	2.6	100	2.5	100	0.7	99
ACN	4.6	91	4	88	4.8	92	5.3	94

Table 3 Recovery values of different solvents (in %) used for DCL (NPR) reconstitution

Solvent	DCL				NPR			
	RSD _{UV/VIS} (%)	R (%)	RSD _{HPLC} (%)	R (%)	RSD _{UV/VIS} (%)	R (%)	RSD _{HPLC} (%)	R (%)
MeOH	2.7	97	8.7	94	4.1	90	3.6	80
H ₂ O	2.5	99	7.8	99	2.8	100	8.4	99
ACN	2.8	99	4.3	100	2.5	99	1.6	100
MeOH/H ₂ O	6	94	9.2	92	3.4	84	9.4	80
ACN/H ₂ O	4.1	99	2.5	99	2.7	100	3.4	100

4.2 Heterogeneous photocatalysis of pharmaceuticals

4.2.1 UV photolysis of the pharmaceuticals

Photolysis is a phenomenon that is completely independent of the presence of the photocatalyst. A series of experiments was conducted to determine the effect of UV-A radiation on the photolytic degradation of the tested drugs. From Figure 1, it is evident UV irradiation was not very effective on drug removal (up to 4% for both of drugs). This is advantageous because most DCL (NPR) loss will be due to photocatalytic decomposition of the drugs. From the analysis of absorption peaks of the drugs and emission spectrum of the lamp, there was minimal absorption in the UV-A region (400–320 nm). Subsequently, the effect of UV photolysis with 0.5 g/L of H₂O₂ was explored, with drug removal being approximately 15% due to the photolytic degradation of the H₂O₂ to hydroxyl radicals.

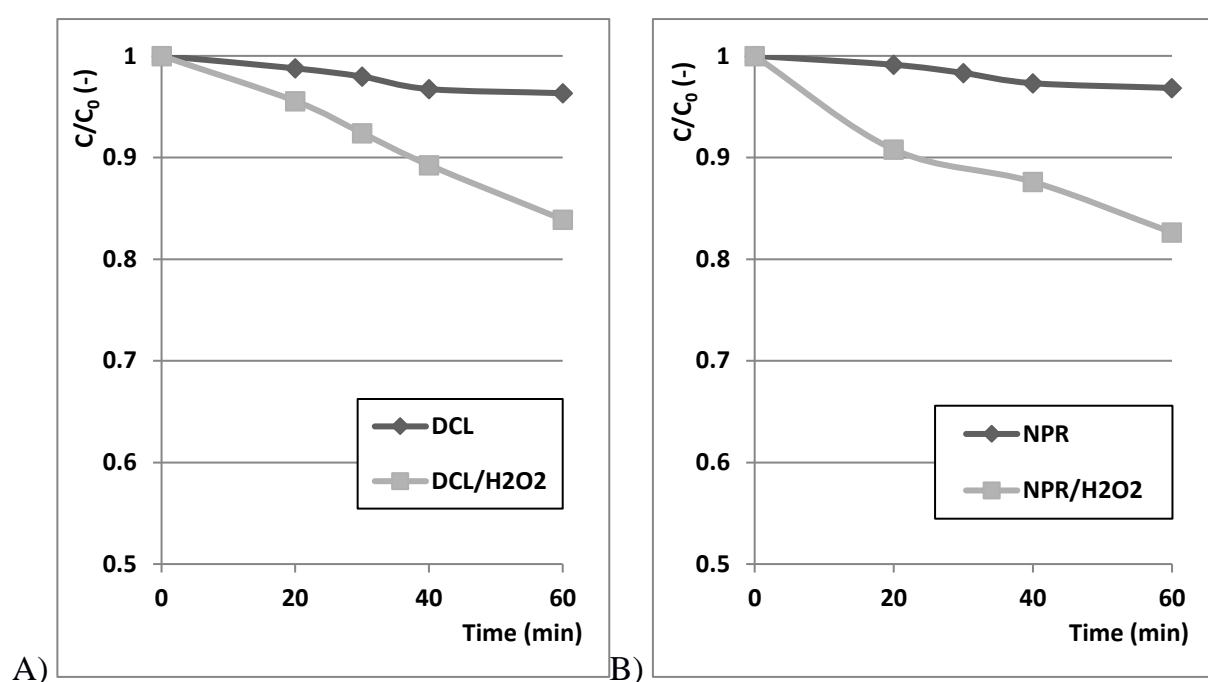


Figure 1 Loss of diclofenac and naproxen by UV photolysis (concentration of each pharmaceutical 500 $\mu\text{g/L}$; 0.5 g/L H₂O₂, matrix: drinking water; pH 6.5)

4.2.2 Photocatalyst and its amount determination

The suitable type and amount of catalyst is a crucial requirement for an effective photocatalytic process. The most suitable catalyst was determined as the AV-01 photocatalyst (see Figure 2A). According to the isoelectric point data, the P-25 photocatalyst is more easily aggregated at a pH of the treated waters (pH = 6.5). Using the mean of aggregated particles and simplistic assumption of the spherical shape of these aggregates, the secondary surface area was calculated. The results showed that the P-25 photocatalyst significantly reduced its specific surface after aggregation, which subsequently slowed the degradation of both drugs.

It can be assumed that the drug is sorbed preferably on the surface of the aggregates, with negligible penetration into the pores of the aggregates and absorption or reflection of UV radiation by the surface, which is why the individual particles within the aggregates are ineffective in terms of influencing the degradation process.

The best results were found for the photocatalyst with the largest secondary surface, ie the AV-01 catalyst. Therefore, all subsequent experiments were performed with this catalyst. At low catalyst concentrations, photodegradation was limited by the total number of active sites on the catalyst surface. In contrast, at high catalyst concentrations, the number of active sites was sufficient, but the process was limited by their availability, i.e. insufficient radiation penetration to all dispersed particles. According to Figure 2B, it is clear that the optimal catalyst concentration was 0.5 g/L for the studied system.

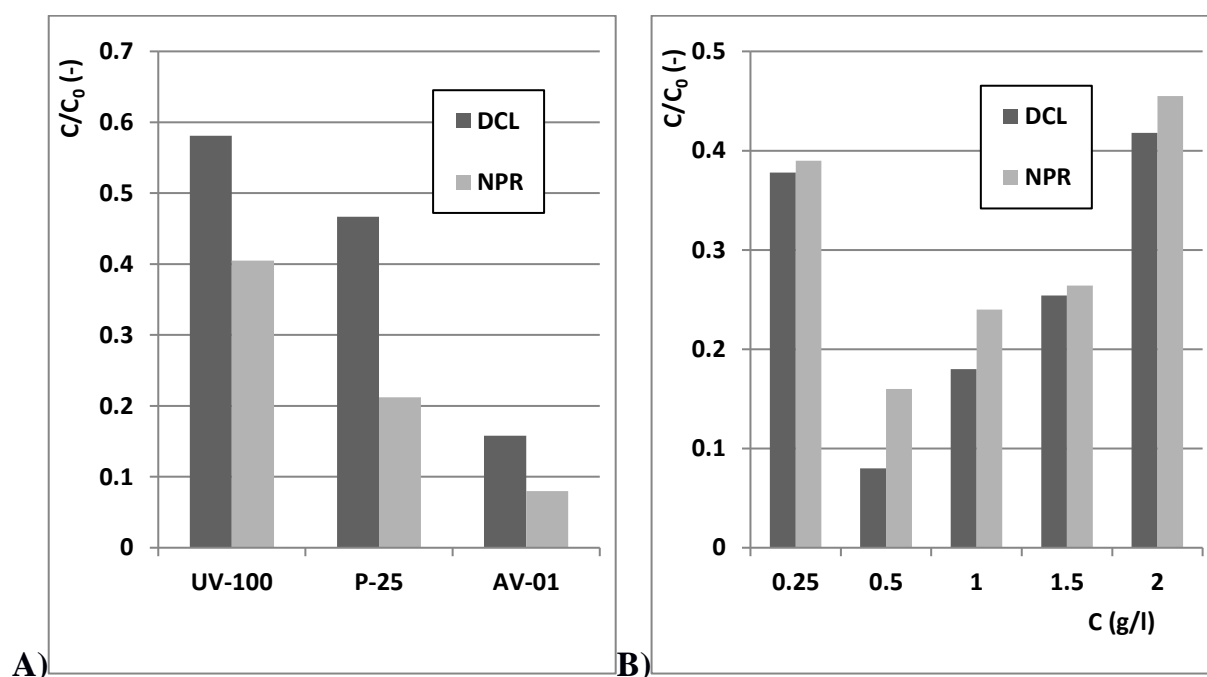


Figure 2 A) Loss of diclofenac and naproxen using photocatalysts UV-100, P-25 and AV-01 (drug concentration 20 mg/L; matrix: drinking water; pH 6.5) B) Loss of diclofenac and naproxen using different concentrations of photocatalyst AV-01 (drug concentration 500 μ g/L; matrix: drinking water; pH 6.5)

4.2.3 Effect of substrate concentration

Substrate concentrations of 500 μ g/L and 20 mg/L were chosen to investigate the effect of substrate concentration, with similar DCL and NPR conversion found for both drug concentrations used. In both cases, over 90% of the DCL and 80% of the NRP were removed as shown in Figure 3.

Table 4 compares quantum yield Φ , rate constant k and half-life $\tau_{1/2}$ for heterogeneous photocatalysis of pharmaceuticals at different concentrations. There was a low quantum yield both for DCL and NPR at a concentration of 500 μ g/L, whereas there was a higher quantum yield for a DCL concentration (NPR) of 20 mg/L. Similarly, the rate constants

k were higher for the concentration of 20 mg/L. The system described is not limited by the content of the drug, nor by the amount of incident photons. According to the results, it would be preferable to remove a higher content of pharmaceuticals. However, from a practical point of view, the reaction must take place at environmentally relevant concentrations, which are often even lower concentrations.

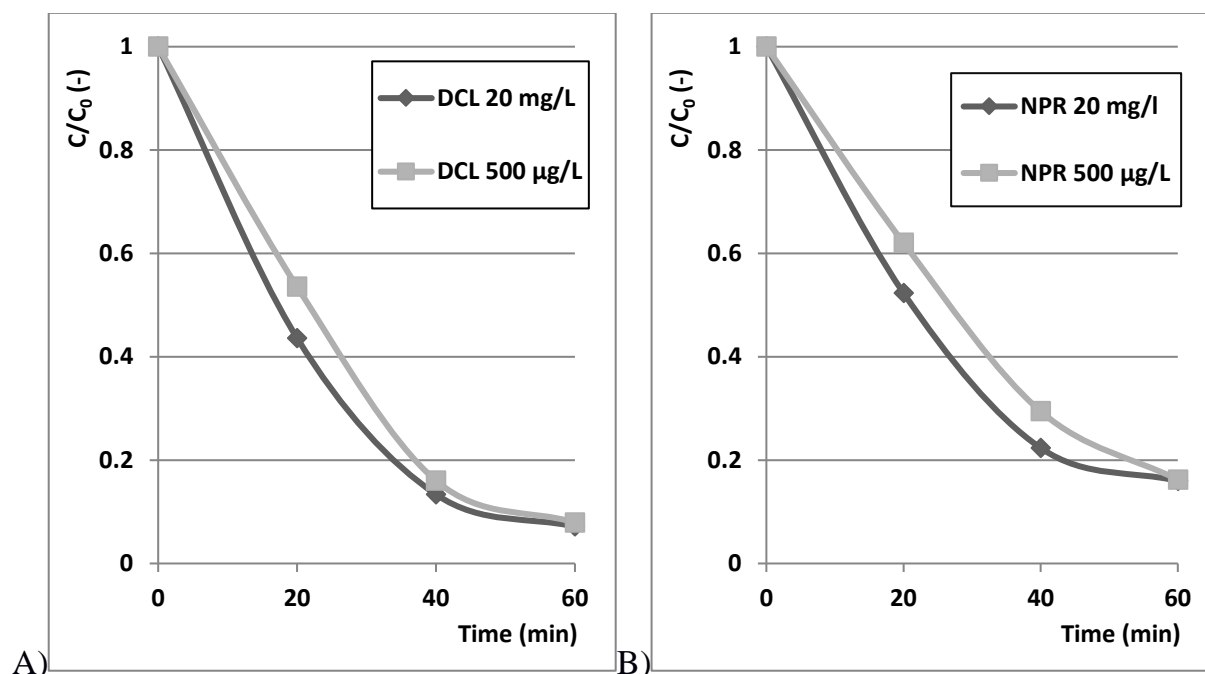


Figure 3 Loss of diclofenac and naproxen by heterogeneous photocatalysis (concentration of each pharmaceutical 20 mg/L a 500 µg/L; matrix: drinking water; pH 6.5)

Table 4 Quantum yield Φ , rate constant k and half-life $\tau_{1/2}$ for heterogeneous photocatalysis of pharmaceuticals at different concentrations

Concentration	Φ		k (min ⁻¹)		R^2		$\tau_{1/2}$ (min)	
	DCL	NPR	DCL	NPR	DCL	NPR	DCL	NPR
500 µg/L	9.16×10^{-5}	10.5×10^{-5}	0.04	0.03	0.99	0.98	16.3	23.3
20 mg/L	0.0036	0.0041	0.05	0.03	0.98	0.99	15.4	23.2

4.2.4 Heterogeneous photocatalysis in real water matrices

Figure 4 shows the conversion of drugs in SW and WW together with heterogeneous photocatalysis of the same amount of drugs in DW. Lower conversions of DCL and NPR were achieved in both matrix types. There was a considerable decrease in the

photocatalytic process observed in the WW matrix, where conversion of both drugs was only 12% for DCL and 9% for NPR. For characterization of matrices, the parameters COD_{Cr} , biochemical oxygen demand (BOD_5), and total organic carbon (TOC) were determined. Table 5 shows the ratios of non-specific parameters after and before photocatalysis of the matrices as well as ratios of 20 mg/L of DCL (NPR) in DiW.

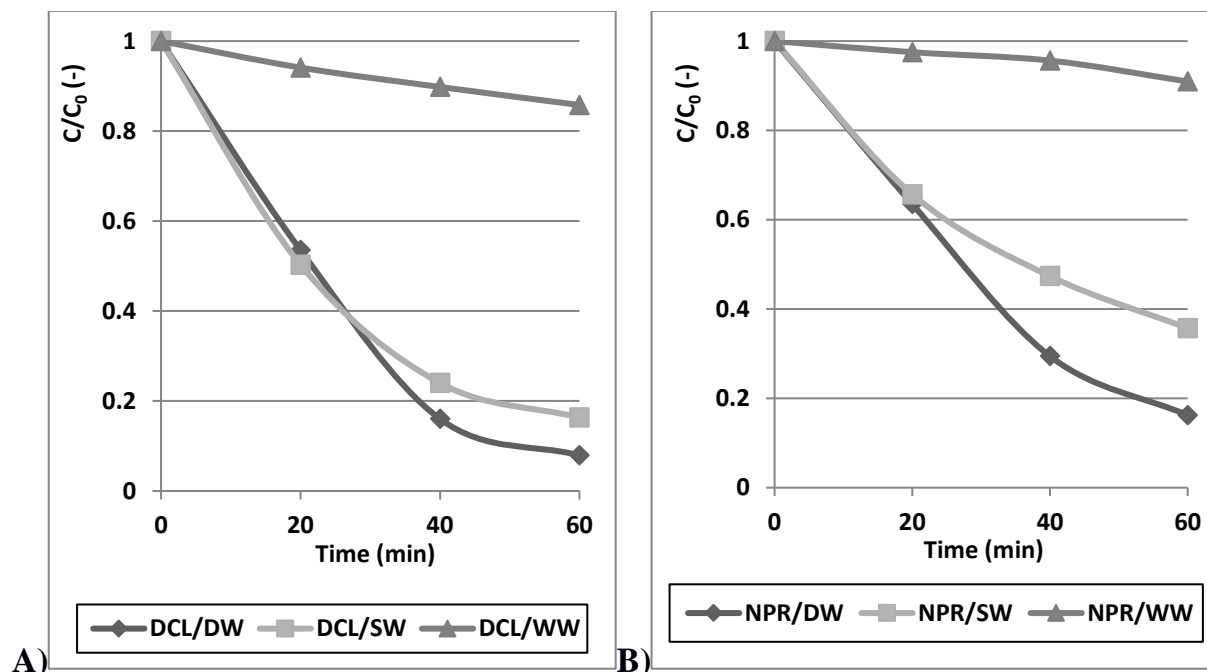


Figure 4 A) Loss of diclofenac by heterogeneous photocatalysis (concentration 500 $\mu\text{g/L}$; matrix: drinking, surface and waste water; pH 6.5) **B)** Loss of naproxen by heterogeneous photocatalysis (concentration 500 $\mu\text{g/L}$; matrix: drinking, surface and waste water; pH 6.5)

The results show that oxidizable substances in the matrices are also subject to photocatalytic reaction, therefore the degradation process is very non-selective. Ratios for the matrices themselves after photocatalytic process are less than one, which means that a certain amount of organic substances are oxidized to CO_2 and H_2O . For drug solutions, there is also evident reduction for COD_{Cr} and TOC ratio, respectively, indicating a partial ability to mineralize these drugs. Furthermore, enhancement of the BOD_5 ratio means that some of the drug is converted to biodegradable degradation products. Thus, it is evident that the decomposition by-products formed during heterogeneous photocatalysis of DCL (NPR) are more readily biodegradable than the original drugs.

Table 5 Ratio of non-specific parameters of surface and wastewater (without drug addition) after 1 hour of photocatalytic process compared to degradation of solution containing 20 mg/L of drugs in deionized water

Parameter	System		DCL	NPR
	SW	WW	20 mg/l	20 mg/l
$\text{COD}_{\text{Cr}}/(\text{COD}_{\text{Cr}})_0$	0,75	0,71	0,65	0,70
$\text{BOD}_5/(\text{BOD}_5)_0$	0,80	0,62	3,0	1,3
$\text{TOC}/(\text{TOC})_0$	0,82	0,71	0,88	0,90

The pH was adjusted to the acidic region to increase the photocatalytic effect in real matrices. It was found that higher conversions were achieved in comparison to samples with untreated pH (Figure 5). The loss of DCL was 87% in SW and 50% in WW, similarly, NPR conversion was 88% in SW and 50% in WW. Also, a higher quantum yield was achieved compared to experiments without pH adjustment. Similarly, the rate constant k also increased with a simultaneous decrease of $\tau_{1/2}$, which is favorable mainly for drugs in the WW matrix, where the $\tau_{1/2}$ decreased from hours to tens of minutes. This phenomenon can be explained by dissociation of drug molecules, consequently by preferential sorption of drug anions to the positively charged surface of the photocatalyst. The adsorption capacity of 49 μg DCL/g catalyst and 36 μg NPR/g was determined in the untreated environment. At pH = 3, the adsorption capacity was 3 to 5 times higher, ie 162 $\mu\text{g}/\text{g}$ for DCL and 198 $\mu\text{g}/\text{g}$ for NPR. In contrast, in the alkaline region (pH = 10), the DCL adsorption capacity was 27 $\mu\text{g}/\text{g}$ and 18 $\mu\text{g}/\text{g}$ for NPR. This decrease can be explained by the repulsive forces between negatively charged drug molecules and the equally charged photocatalyst surface.

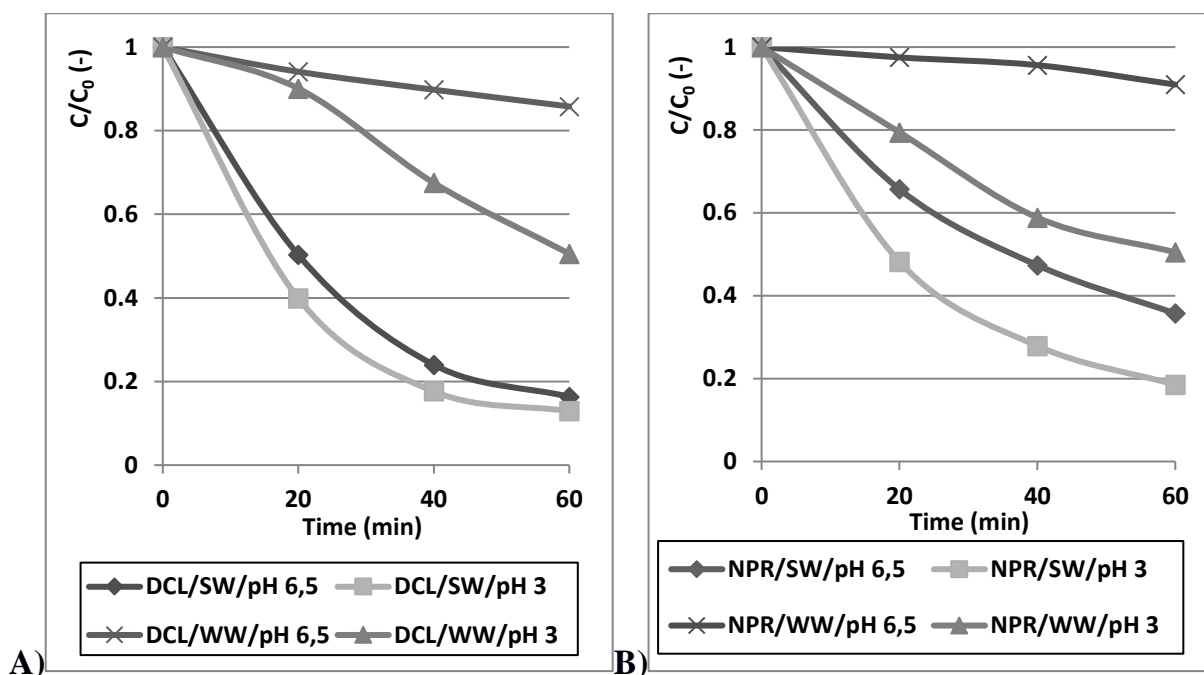


Figure 5 A) Loss of diclofenac by heterogeneous photocatalysis (concentration 500 $\mu\text{g/L}$; matrix: surface and waste water; pH 3) B) Loss of naproxen by heterogeneous photocatalysis (concentration 500 $\mu\text{g/L}$; matrix: surface and waste water; pH 3)

A series of experiments was also conducted to determine the effect of 0.5 g/L H_2O_2 on the removal of DCL and NPR from aqueous solutions. Figure 6 shows a higher efficiency of pharmaceuticals removal compared to the photocatalytic effect without H_2O_2 . Furthermore, it is evident that the DCL conversion was more than 90% in SW and 70% in WW, with a NPR conversion of 80% in SW and 61% in WW. The rapid increase in the degradation efficiency of both drugs occurred mainly in the matrix formed by WW, suggesting that the addition of H_2O_2 to the reaction mixture may be a significant intensification factor for the entire degradation process.

As previously discussed, H_2O_2 can act on organic substances present in matrices in several ways, direct oxidation of low molecular substances, participation during their photolysis, or complex photocatalytic decomposition may occur. Previous experiments show that the drugs of interest are degraded mainly by hydroxyl radicals generated by the photocatalytic process. However, simpler organic compounds present in matrices can also be effectively degraded by the first two mentioned mechanisms running simultaneously during the photocatalytic process. As a result, sorption of organic substances on the surface of the catalyst decreases to such a level that a higher sorption of the molecules of drugs is possible.

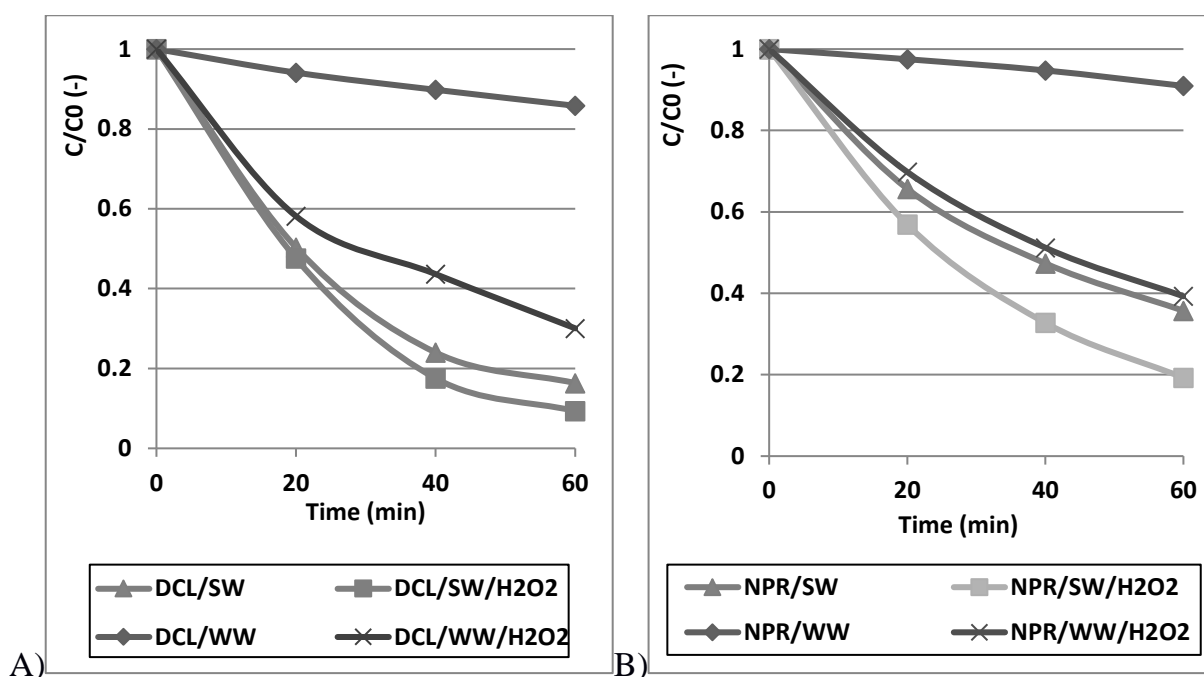


Figure 6 A) Loss of diclofenac by heterogeneous photocatalysis (concentration 500 $\mu\text{g/L}$; concentration of H_2O_2 0.5 g/L; matrix: surface and waste water; pH 6.5) B) Loss of naproxen by heterogeneous photocatalysis (concentration 500 $\mu\text{g/L}$; concentration of H_2O_2 0.5 g/L; matrix: surface and waste water; pH 6.5)

The possible additive effect of acidification to pH 3 and addition of H_2O_2 during heterogeneous photocatalysis of pharmaceuticals was explored. Over 95% of DCL and over 90% of NPR in SW and 90% of DCL and 80% of NPR in WW were removed during the experiment as can be seen in Figure 7. Heterogeneous photocatalysis in combination with pH adjustment or addition of H_2O_2 to the treated water has been shown to affect changes in drug concentration and other substances of the water matrix in which they occur as well. These processes are generally considered to be non-selective, however, from the experiments, it is apparent that a suitable reaction mixture composition can shift the conversion in the desired direction.

Table 6 shows a comparison of the quantum yield Φ , rate constant k_p and half-life $\tau_{1/2}$ for the individual drugs in different matrices, with and without addition of peroxide and with acidification. These data suggest that the addition of H_2O_2 and acidification results in a higher quantum yield and rate constant values compared to untreated systems, especially in waste water matrices. In this system, $\tau_{1/2}$ declined from several hours to tens of minutes.

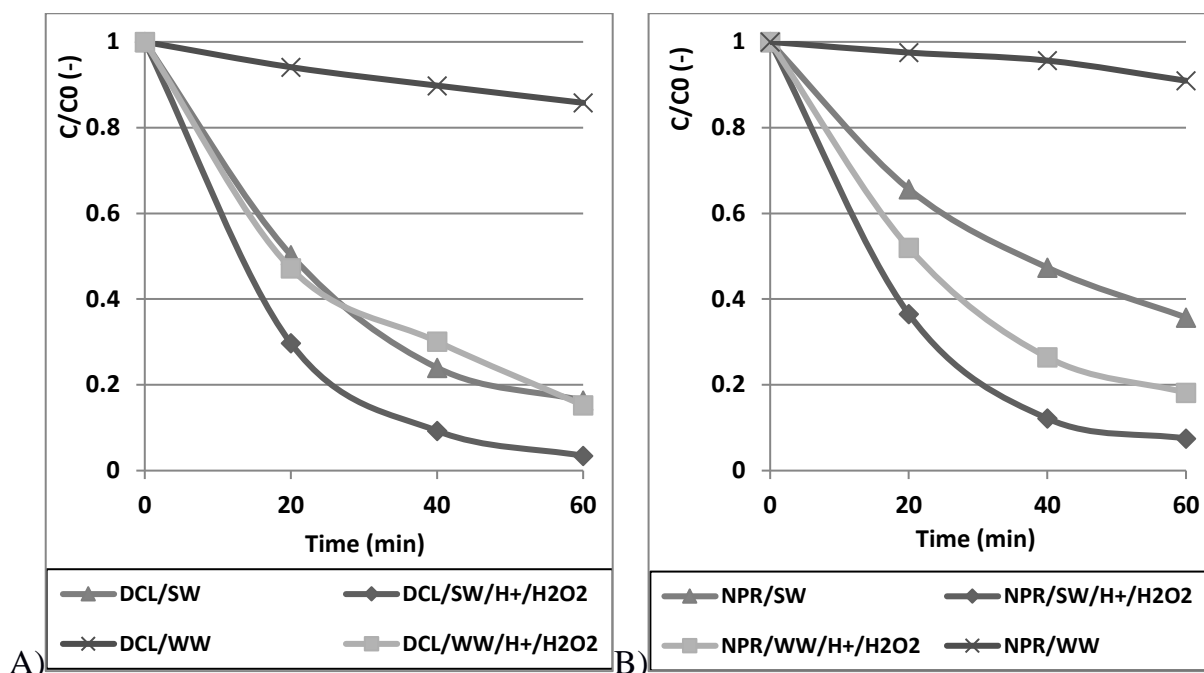


Figure 7 A) Loss of diclofenac by heterogeneous photocatalysis (concentration 500 $\mu\text{g/l}$; concentration of H_2O_2 0.5 g/L; matrix: surface and waste water; pH 3) **B)** Loss of naproxen by heterogeneous photocatalysis (concentration 500 $\mu\text{g/L}$; concentration of H_2O_2 0.5 g/L; matrix: surface and waste water; pH 3)

Table 6 Comparison of quantum yield Φ , rate constant k_p and half-life $\tau_{1/2}$ for various modifications of photocatalytic experiments (concentration of each pharmaceutical 500 $\mu\text{g/l}$ in drinking, surface and waste water)

Process	Φ ($\times 10^{-5}$)		k_p (min^{-1})		R^2		$\tau_{1/2}$ (min)	
	DCL	NPR	DCL	NPR	DCL	NPR	DCL	NPR
DW	9.16	10.5	0.0425	0.0299	0.99	0.99	16.3	23.3
SW	8.3	8.2	0.0321	0.0179	0.98	0.99	21.6	38.7
WW	1.2	1.1	0.0026	0.0016	0.99	0.98	266.6	462.1
DW/ H^+	9.9	11.7	0.077	0.043	0.99	0.97	9.9	17.3
SW/ H^+	8.7	11.1	0.037	0.029	0.95	0.99	18.7	20.4
WW/ H^+	4.9	6.3	0.011	0.012	0.95	0.99	38.5	63.0
DW/ H_2O_2	9.9	11.5	0.094	0.039	0.97	0.99	9.5	17.2
SW/ H_2O_2	9.1	8.8	0.041	0.028	0.99	0.98	15.6	28.9
WW/ H_2O_2	6.9	7.8	0.026	0.016	0.98	0.99	33.5	43.1
DW/ $\text{H}^+/\text{H}_2\text{O}_2$	9.9	11.5	0.091	0.038	0.99	0.97	9.9	17.3
SW/ $\text{H}^+/\text{H}_2\text{O}_2$	8.8	11.4	0.057	0.048	0.99	0.98	12.2	14.4

Process	Φ ($\times 10^{-5}$)		k_p (min^{-1})		R^2		$\tau_{1/2}$ (min)	
	DCL	NPR	DCL	NPR	DCL	NPR	DCL	NPR
WW/H ⁺ /H ₂ O ₂	8.1	10.2	0.031	0.03	0.99	0.98	22.4	23.1

4.3 Toxicity of pharmaceuticals and its by-products

Although promising experimental results have been achieved describing the photocatalytic destruction of both drugs, several intermediates can be produced with even more toxicity than the original drug. Comparing the TOC, COD_{Cr} and BOD₅ values, it is clear that the degree of mineralization of DCL and NPR is relatively low (see Table 5), whereas the biodegradability of the drug mixture and its intermediates has increased. However, the lower COD_{Cr}/BOD₅ ratio does not necessarily mean a reduction in DCL and NPR toxicity to non-target organisms. For this reason, the toxicity to *Parachlorella kessleri* was investigated.

The results show that inhibition of the growth of *Parachlorella kessleri* is negligible (up to 5%) at a concentration of 500 $\mu\text{g/l}$, whereas the WW itself showed a phytotoxic effect to *P. kessleri* (37%). However, wastewater samples after heterogeneous photocatalysis showed reduced growth inhibition (11%) and the growth inhibition of algae in SW was 6.3%. After the photocatalytic process, there was a decrease in toxicity to 1%, with similar results obtained for 500 $\mu\text{g/l}$ DCL in these matrices, as shown in Table 7.

DCL (NPR) in DW showed similar growth rates as control samples. Similarly, at such a low drug concentration, it was not clear whether more toxic intermediates were generated from the original DCL or NPR molecule. Therefore, a concentration of 20 mg/L of DCL (NPR) was used, showing the toxic effect of these drugs. Growth inhibition of *P. kessleri* was 62% for DCL and 25% for NPR, which gradually reduced during the photocatalytic process as shown in Figure 8.

Table 7 Growth inhibition (in %) of *Parachlorella kessleri* alga in surface and waste water matrices before and after heterogeneous photocatalysis (drug concentration 500 $\mu\text{g/L}$)

Time (min)	SW		WW		SW	WW
	DCL	NPR	DCL	NPR		
0	12.3	12.5	44.9	42.4	6	38
60	1.3	4.5	8.5	19.5	1	11

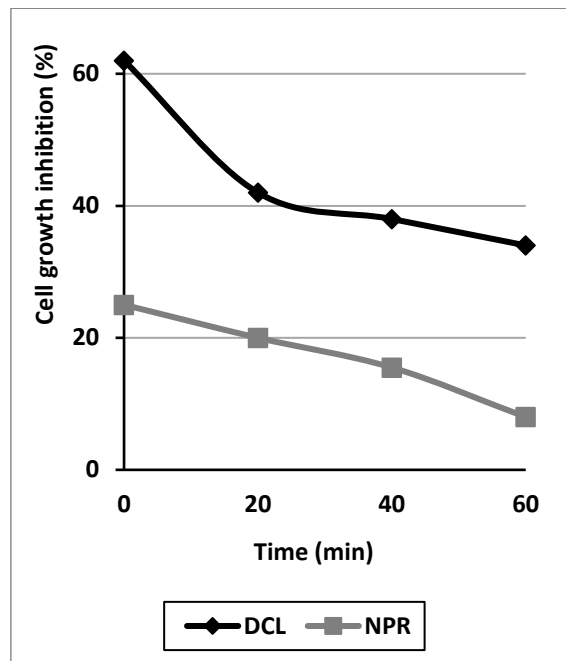


Figure 8 Growth inhibition of *Parachlorella kessleri* alga in drug-containing water samples during heterogeneous photocatalysis (drug concentration 20 mg/L, matrix: drinking water)

5 Conclusion

This dissertation investigated the photocatalytic removal of diclofenac and naproxen residues from water, whose environmental risks are considerable. The results of extensive laboratory experimental studies are summarized as follows:

- It was found that the NSAIDs pharmaceuticals diclofenac and naproxen were effectively removed by heterogeneous photocatalysis with an anatase type TiO₂ photocatalyst. The effective source of radiation was a low energy UV-A LED source with a wavelength of 365 nm and photon flux of 4.71 μEs/s.
- The effect of direct photolysis was negligible, and the main degradation process was decomposition by hydroxyl radicals emerging in the photocatalytic system.
- High photoactivity was found in commercially available TiO₂ AV-01, as unlike other photocatalysts, it does not aggregate at neutral pH.
- A suitable reaction mixture composition can, to some extent, increase the conversion of the removed drugs. The degradation rate was significantly influenced by the pH of matrix, as it predetermines the charge of the catalyst particles, consequently the adsorption of the substrate on the catalyst surface. The presence of H₂O₂ in the reaction mixture increased the rate of degradation, while the UV/TiO₂/H⁺/H₂O₂ system showed the highest efficiency.
- A high reduction of the concentration of drug residues was also achieved in real river and wastewater matrices, although the conversion was affected by the presence of organic substances in individual matrices. This phenomenon is due to the non-selective behavior of hydroxyl radicals. Thus, this method also removes substances that can be easily degraded, for example, in the biological stage of wastewater treatment, whereas the photocatalytic processes can be used, for example, in the final stage of water purification to remove residual organic contamination.
- Under the experimental conditions using the UV-A LED source, no toxic diclofenac and naproxen degradation intermediates were formed. Similarly, the biodegradability of the reaction mixture after photocatalytic process increased.
- To enable determination of extremely low concentrations of drugs, the method for the effective treatment of drug samples by the SPE was modified and verified. A 1:1 mixture of ACN with MeOH was used as eluent, with deionized water used for reconstitution, providing a high yield even for highly heterogeneous samples (wastewater).

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7 List of Students' Published works

7.1 Publications in journals with IF

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7.3 Contributions presented at international scientific conferences

- **TROUSIL V.**, BLAŽKOVÁ Z., SLEHOVÁ E., MACHALICKÝ O., PALARČÍK J., CAKL J., Study of naproxen and diclofenac removal in model

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- **TROUSIL V.**, PALARČÍK J., BLAŽKOVÁ Z., KOŘÍNKOVÁ J., MACHALICKÝ O., CAKL J., Removal of nonsteroidal anti-inflammatory drugs by heterogeneous photocatalysis, *69. Zjazd chemikov*, Vysoké Tatry, 11. - 15. 9. 2017, pp. 206, ISSN: 1336-7242.
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7.4 Contributions presented at national scientific conferences

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7.5 Projects

- Member of the research team of project TH02030823 “Development of methodological and technical procedures for minimizing the impact of forest management on groundwater quality due to excessive migration of reactive forms of nitrogen and phosphorus”, 2017–2018.