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Solar-Driven Degradation of Ciprofloxacin in the Aquatic Environment

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ABSTRACT

Ciprofloxacin (CIP), a pharmaceutical compound, -occurs as a micropollutant in various types of environmental matrices including wastewater, because it is resistant to removal via conventional methods - due to its persistent characteristics. For this reason, in this work the efficiency of photodegradation CIP (2 mg L^{-1}) in Milli-Q water (MW) and tap water (TP) was investigated using TiO_2 and ZnO at a concentration of 20 mg L^{-1} each. The tests were performed without and in the presence of SO_4^{2-} ions (250 mg L^{-1}) as one of main components of the aquatic, environmental matrices. Solar-driven photocatalysis using TiO_2-P25 and ZnO improved the removal efficiency of CIP compared to its solar photolysis. In all cases approximately 90% removal of CIP was observed after 20 to 30 minutes, but no mineralization processes was achieved. The most efficient degradation was obtained using TiO_2 at concentration of 20 mg L^{-1} in DW without the presence of SO_4^{2-} after 5 minutes. The photodegradation rate constants estimated $k_t = 0.644$ min^{-1} and $k_{QUV} = 0.249$ L kJ^{-1}. The complexity of the matrix affected the efficiency of CIP removal, favouring DW. The impact of sulfate anions also depended on the matrix: in distilled water, their impact was negative on the photocatalysis process efficiency, while in tap water, they slightly accelerated a process of CIP decomposition. Taking this into account, photocatalysis is an efficient; however, further research is necessary.

Keywords: zinc oxide, photocatalysis, titanium dioxide, ciprofloxacin, anions.

INTRODUCTION

Occurrence of the antibiotics in the aquatic environment is an urgent problem. Due to the overuse of antibiotics for medical, veterinary and agricultural purposes and their resistance to biodegradation, they are constantly detected in environmental samples [Triquet et al., 2020; Kraemer et al., 2018]. The environmental contamination by antibiotics may cause major threat to human health and ecological risks such as spreading of antibiotic-resistant bacteria (ARB) and antibiotic-resistant genes (ARGs), adverse effect on various aquatic organisms or accumulation in soil, plants and animals tissues [Trakulmututa et al., 2022]. Conventional wastewater treatment plants (WWTPs), and in particular effluents from these systems, are suspected to be – one of the main source of the antibiotics, ARB and ARGs in the aquatic environment. Due to inefficient removal of these microcontaminants and lack of control over ARB and ARGs spreading, antibiotics residues are continuously released into environmental reservoirs [Kowalska et al., 2020; Rizzo et al., 2013]. Ciprofloxacin (CIP) is a broad spectrum antibiotic and extensively used as human and veterinary medicine from the fluoroquinolones group (FQs) [Duong et al., 2008]. It was reported that CIP is detected in both influent and effluent of WWTPs. The effluents from WWTPs are introduced into the aquatic environment, leading to the widespread presence and frequent detection CIP and other micropollutants in groundwater, surface water, sewage, and seawater globally [Chen et al., 2017]. CIP was detected in river sediment [Agunbiade and Moodley, 2016], river water [Azanu et al., 2018; Gavrilescu et al., 2015], groundwater [Ma et al., 2015] and tap water

[Hanna et al., 2018] at various levels between 0.4–1300 ng L^{-1}. For this reason, there is a need to look for more efficient and economical methods of removing antibiotics.

Advanced oxidation processes (AOPs), especially heterogeneous photocatalysis is very often mention to be an effective, eco-friendly and cost effective method for micropollutants degradation [Karuppaiah et al., 2019]. Irradiated semiconductor photocatalysts undergo charge separation and further generate reactive oxygen species (ROS) such as hydroxyl radicals (·OH), superoxide radicals ($\cdot O_2^-$) and hydrogen peroxide (H_2O_2) [Torres-Palma et al., 2019]. Semiconductors have been widely used as photocatalysts, particularly titanium dioxide (TiO_2), with wide bandgap between (3.2 eV) depending on the crystalline phase, which presents remarkable properties, including low cost, high stability, low toxicity, and high photocatalytic efficiency in degrading multiple organic contaminants [Byrne et al., 2017; Kurt et al., 2017]. In turn, zinc oxide (ZnO) is also a semiconductor with a broad band gap in the near-UV spectral region and is renowned for its large free-exciton binding energy and high oxidation activity in photocatalytic removal of various organic pollutants [Karuppaiah et al., 2019; Wolski et al., 2021]. The efficiency of a photocatalytic slurry system primarily relies on irradiation, catalyst dosage, initial concentration of pollutants, the physical-chemical traits of wastewater (e.g., pH and dEfOM) and complexity of the environmental matrix [Rizzo et al., 2019]. The presence of organic and inorganic particles in water such as humic acids, radical scavengers like cations, and anions, can cause adverse effect on the efficiency of the process [Gupta et al., 2021] such as: (i) scavenging of hydroxyl radicals by anions and producing radicals with lower oxidation potentials; (ii) adsorption onto catalyst surface of some organic and inorganic species [Rizzo et al., 2019].

The aim of the study was to assess the removal efficiency of CIP from distilled water (DW) and tap water (TW) by photocatalysis initiated by sunlight using two photocatalysts as TiO_2 and ZnO. The experiments were carried out also in the absence and presence of sulfates (SO_4^{2-}), as one of the main anions naturally occurring in environmental matrices.

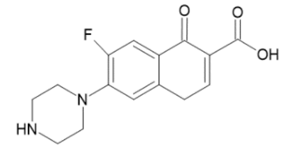
MATERIALS AND METHODS

Reagents and chemicals

CIP (98%) was purchased from Sigma Aldrich (China) and the main information on this compounds was listed in Table 1. Acetonitrile (ACN) and formic acid (FA) with HPLC-grade (99.9%) used for chromatographic analyses were purchased from Sigma-Aldrich (Poland). Milli-Q water was used throughout the study. Studied photocatalysts: TiO_2-P25 (Titandioxid P25, 99,9%) and ZnO with high purity (99.9%) were supplied by Degussa (Germany) and Sigma-Aldrich (China), respectively. Na_2SO_4 (99%) was purchased from Avantor Performance Materials (Poland).

A standard solution of CIP (10 mg L^{-1}) was prepared by dissolving 10 mg of its analytical standard in 1000 mL water. It was stirred through 16 h in volumetric flask until the analytical standard was completely dissolved. Working standard solutions in the concentration of 2 mg L^{-1} was prepared by dilution of 200 mL standard solutions in Milli-Q water to appropriate concentrations immediately before the use. Standard solution was kept in the refrigerator (1 °C) and were stable at least 3 weeks.

Table 1. Main chemical and physical properties of CIP

Parameter	CIP
Molecular formula	$C_{17}H_{18}FN_3O_3$
Structure	
Molecular weight, g mol^{-1}	331.34
Dissociation constant	pKa_1 = 6.16 pKa_2 = 8.62
$\log K_{ow}$	0.28
Solubility in water, mg L^{-1}	30.0 (at 20 °C)

Matrices

In the studies, two aquatic matrices were selected for the tests, i.e.: Milli-Q water (MW) and tap water (TW). MW obtained from the Synergy® Water Purification System (Merck, Germany) Its resistivity was 18.2 MΩ.cm at 25 °C and conductivity ≤ 5 µS. Characteristics of the TW matrix presents in the table (Table 2). The matrices were spiked with CIP at a concentration

Table 2. Chemical and physical properties of TW

Parameter	TW
COD, mg L^{-1}	12
TOC, mg L^{-1}	1.54* ± 0,2
TN, mg L^{-1}	63.97 ± 0.07
$N\text{-}NO_2$, mg L^{-1}	ND
$N\text{-}NO_3$, mg L^{-1}	7.11 ± 6.5
$P\text{-}PO_4$, mg L^{-1}	ND
Br^-, mg L^{-1}	0.3 ± 5.2
F^-, mg L^{-1}	0.24 ± 5.1
Cl^-, mg L^{-1}	72.72 ± 5.6
SO_4^{2-}, mg L^{-1}	144.55 ± 4.0
pH	7.62 ± 0.01

Note: ND – not detected, * – NPOC method measurement.

of 2 mg L^{-1}. The determination of the CIP concentration was conducted through experimental means. Following instrumental analysis utilizing HPLC, concentration of 2 mg L^{-1} was deemed most suitable due to its capacity for quantifying the targeted compound.

Analytical measurement

HPLC analysis

Quantification of CIP was performed by High-Performance Liquid Chromatography (HPLC) coupled with a UV variable wavelength detector (UltiMate 3000 system; Dionex Corporation, Sunnyvale, CA, USA). All samples were filtered using MCEMF-Millipore® Membrane Filters with 0.22 µm pore size (Merck, Germany). The chromatographic separation was performed using a C18 Hypersil™ Gold column (250 mm x 4.6 mm; pore size: 5 mm) (Thermo Scientific, Polygen, Poland). The mobile phase was consisted of 0.1% FA solution and ACN in a volumetric ratio of 77:23 (v/v). The analyses were carried out at 278 nm, corresponding to the maximum absorption of CIP. The retention times (RT) of the target contaminant was equal to 9.3 ± 0.5 min. The limit of quantification (LOQ) of studied antibiotic was equal to 0.2 mg L^{-1}. It was established as the first lowest calibration point of their calibration curves (linear regression, $R^2 > 0.98$). The data were elaborated using Dionex Chromeleon™ 6.8 software.

Physicochemical measurements

Total organic carbon (TOC) was determined in the filtered environmental samples using TOC-L Total Organic Carbon Analyzer (Shimadzu, Japan). Total nitrogen (TN) was measured using TNM-L Total Nitrogen Measuring Unit (Shimadzu, Japan). Other chemical properties of TW were analysed using Ion Chromatography Dionex Aquion (Thermo Scientific, Poland). Chemical oxygen demand (COD) was analysed using spectrometer Spectroquant NOVA 60TM (Merck, Germany) and spectrophotometric test (no. 114540) purchased from Merck (Germany).The pH of environmental samples was measured by pH-meter Multi 3401 (WTW, Germany).

Experimental set-up

Laboratory-scale experiments on the removal of CIP from aquatic matrices (MW, TW) by means of artificial sunlight were performed in a solar radiation simulator Solarbox 1500 e system (Co.fo.me.gra, Italy) equipped with a 1500 W polychromatic Xenon lamp. The studies were carried out at light irradiation equalled to 500 W m^{-2} specified as average insolation for the 52nd parallel north, which crosses Poland at noon in the spring and autumn months [Felis et al., 2016]. The experiments on solar-driven photocatalytic removal of CIP were performed with the presence of photocatalysts: TiO_2-P25 (P25, 99.9%, Degussa, Germany), and ZnO (99.9%, Sigma-Aldrich, Poland) at a concentration of 20 mg L^{-1}. SO_4^{2-} was used at concentration of 250 mg L^{-1}, which is the highest permissible concentration according to European Union Directive [EU, 2020]. SO_4^{2-} were selected for study as one of the primary anions due to their widespread presence in aquatic environment and their potential impact on the efficiency of antibiotic photodegradation processes. The total volume of the treated medium equalled 250 mL and the irradiated area was 0,03 m^2. The working solution were constantly stirred during the experiment. Samples were taken at the following time points: 0 min, 5 min, 10 min, 20 min, 30 min, 45 min, 60 min and 90 min. The solar irradiance was controlled by spectrometer BLACK-Comet Stellar Net UV–VIS (StellarNet, Florida, USA).

Control tests

Sorption tests

Some substances tend to be sorbed on the surface of photocatalysts. To determine the scale of this phenomenon in the case of CIP, the so-called control tests in dark conditions were performed. The control tests under dark conditions were investigated to assess the removal of the CIP by sorption to the surface of the photocatalyst. Experiments were performed in beakers tightly covered with aluminium foil to limit the potential exposure of the samples to sunlight. The total volume of the treated solution was 250 mL. Sorption tests were carried out at two concentrations of the studied photocatalyst: 20 mg L^{-1}, corresponding to the concentration in the photocatalytic test. The solutions of CIP and photocatalysts with/without SO_4^{2-} at concentration of 250 mg L^{-1}, were mixed on magnetic stirrers. The experiment lasted 60 minutes, during which samples were taken at the same time points as in case photocatalytic experiments.

Photolysis

In order to check the susceptibility of CIP to decomposition under the influence of only sunlight (without the addition of a photocatalyst), studies on the photolytic decomposition of this compound were carried out.. The experiments were performed in a Solarbox 1500 e solar simulator under the same conditions as the photocatalytic processes mentioned above (irradiance: 500 W m^{-2}, the total volume of the treated medium: 250 mL, and irradiated area: 0,03 m^2), but without any photocatalysts additions. The effect of artificial solar irradiance on the removal of CIP was investigated for all selected matrices spiked with CIP at a concentration of 2 mg L^{-1}. Control tests under light conditions were investigated in absence and in the presence of SO_4^{2-} at concentration of 250 mg L^{-1}. Samples were collected at the following time points: 0 min, 5 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min, and 90 min.

Data analysis

The removal efficiency of antibiotics (R) was calculated using the following Eq. 1:

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

where: C_0 and C_t – the initial and the residual concentrations of the antibiotics at t time (mg L^{-1}), respectively.

Cumulative energy (Q_{UV}) was determined according to Eq. 2, based on the spectrometer results.

$$Q_{UV,n+1} = Q_{UV,n} + \overline{UV}_{G,n+1} \cdot \frac{A_i}{V_t} \cdot \frac{\Delta t_n}{1000}; \quad \Delta t_n = t_{n+1} - t_n \tag{2}$$

where: $Q_{UV,n+1}$, and $Q_{UV,n}$ – the cumulative UV energy per volume unit of the treated medium at times n and n-1, respectively (kJ L-1); – the average incident solar UV irradiance measured in time interval Δt_n (W m^{-2}); A_i – the irradiated area (m^2); V_t – the total volume of the treated medium (L), Δt_n – represents the moments in time when samples are collected (s).

The degradation kinetics of CIP was explained by first-order kinetic model. The kinetic model by photocatalytic degradation is presented by Eqs. 3–6.

$$ln\left(\frac{C_{CIP,t}}{C_{CIP,0}}\right) = k_t t \tag{3}$$

where: $C_{CIP,t}$ and $C_{CIP,0}$ – the concentrations of CIP (mg L^{-1}) at time t and time zero, respectively; k_t – the pseudo-first-order rate constant of CIP photodegradation (min^{-1}), t – time (min).

The time needed to achieve 50% photolytic or photocatalytic removal of CIP ($t_{50\%}$, min) was estimated according to Eq. 4 based on the calculated pseud-first-order rate constant k_t.

$$t_{50\%} = \frac{ln2}{k_t} \tag{4}$$

Due to importance of cumulative energy in solar-driven processes, the degradation of CIP can be also represented through a pseudo-first-order reaction by replacing time (t) with the cumulative energy (Q_{UV})(Eq. 5) [Kowalska et al., 2020].

$$ln\left(\frac{C_{CIP,t}}{C_{CIP,0}}\right) = k_t Q_{uv} \tag{5}$$

where: k_{QUV} – the pseudo-first-order rate constant of CIP degradation (L kJ^{-1}), Q_{UV} – cumulative energy (kJ L^{-1}).

Based on the calculated constant rate k_{QUV}, the cumulative energy needed to achieve 50% photolytic or photocatalytic removal ($Q_{UV’50\%}$, kJ L^{-1}) was determined according to Eq. 6.

$$Q_{UV,50\%} = \frac{ln2}{k_{Q_{UV}}} \tag{6}$$

RESULTS AND DISCUSSION

Sorption test

The removal efficiency of CIP by sorption to the surface of TiO_2-P25 and ZnO under dark conditions (control test) depends on matrix complexity and type of photocatalysts. CIP was removed from DW by sorption to particles of TiO_2 and ZnO, and the average removal efficiency was 19.8% and 12.2%, respectively. In case of TW, the CIP was removed by sorption to ZnO particles with very low final efficiency of 4.5%. The average sorption of CIP on the particles of TiO_2 was insignificant and did not exceed 2.3%. However, as the Figure 1 shows, CIP underwent sorption and desorption processes in both cases.

Photolysis

Photolysis of CIP was carried out to assess the degradation efficiency of CIP under only solar radiation. Removal of the CIP from MW was approx. 85% in 10 minutes without SO_4^{2-} and over 90% in the present of these anions (Figure 2). The photolytic degradation rate constant of CIP in absence of SO_4^{2-} equalled to k_t = 2.567 min^{-1} and k_{QUV} = 11.09 L kJ^{-1}, while the time and energy required to achieve 50% removal of CIP was $t_{50\%}$ = 0.27 min and $Q_{UV,50\%}$ = 0.063 kJ L^{-1}, respectively (Table 3). In case of tests conducted with SO_4^{2-}, photolytic degradation rate constant was k_t = 2.288 min^{-1} and k_{QUV} = 9.888 L kJ^{-1}. Degradation efficiency of CIP from TW was less efficient than from MW, because the same removal was achieved after 20 minutes under only sunlight (Figure 2B). The photolytic degradation rate constants of CIP amounted to k_t = 4.002 min^{-1}, k_{QUV} = 17.285 L kJ^{-1} and k_t = 4.068 min^{-1}, k_{QUV} = 17.593 L kJ^{-1} for test without and in the present of SO_4^{2-}, respectively (Table 3). In all cases, the degradation of CIP through photolysis resulted in the formation of by-products.

TOC was measured using NPOC method. During the photolysis in MW without/in the presence of SO_4^{2-}, - no loss in TOC concentrations was observed, which suggests that the mineralization of the CIP did not take place and the removal the compound from water under exposition to sunlight is related to compounds' transformation to by-products. The reason behind the issue may be the transformation of CIP into more stable and non-pourable by-products during photooxidation process.. In case of photolysis in TW, TOC was slightly decreased, and the reason may be presence of organic matter in water, and its decomposition during process. However the presence of SO_4^{2-} reversed this trend.

Photolysis is an important process, particularly for the degradation of micropollutants, such as antibiotics, directly in the environment. Frequently, these contaminants resist degradation through photolysis from MW, displaying

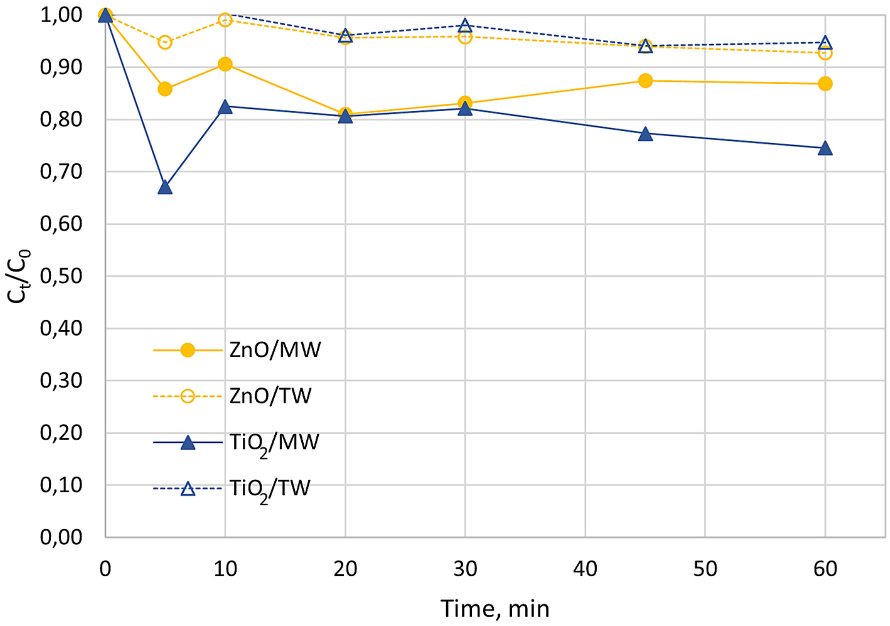


Figure 1. Removal of CIP from MW and TW by sorption on the selected photocatalysts TiO_2-P25 and ZnO

notable inefficiency in the process, where the CIP concentration is almost unchanged under light irradiation in the absence of the catalysts [Zheng et al., 2018]. The study results concerning the elimination of CIP from environmental waters like river water or real wastewater, present different degradation rates from 10 to > 90% at the end of the process [Malakootian et al., 2020; Sturini et al., 2012which resolves difficulties related to separation of catalysts from the solution in the application of sole nanoparticles as well as reusability of nanoparticles. Application of nanoparticles without immobilization on a support medium causes toxic effects in aqueous solutions, which was fixed through immobilization on a glass plate in this study. In

Table 3. Kinetic parameters for the CIP photodegradation

Pseudo-first order kinetic parameters (k, $t_{1/2}$) and correlation coefficient (R^2) of CIP photodegradation estimated for time						
Process	CIP					
	MW			TW		
	k, min^{-1}	$t_{1/2}$, min	R^2	*k*, min^{-1}	$t_{1/2}$, min	R^2
Photolysis	0.187	3.709	0.98	0.117	5.94	0.97
Photolysis // SO_4^{2-}	0.2134	3.244	0.99	0.115	6.012	0.96
ZnO	0.227	3.06	0.87	0.114	6.102	0.93
ZnO // SO_4^{2-}	0.24	2.901	0.93	0.122	5.696	0.94
TiO_2	0.644	1.077	1	0.112	6.167	0.96
TiO_2 // SO_4^{2-}	0.225	3.088	0.96	0.117	5.95	0.97
Pseudo-first order kinetic parameters (k, $t_{1/2}$) and correlation coefficient (R^2) of CIP photodegradation estimated for cumulative energy (Q_{UV}).						
Process	k_{QUV}. L kJ^{-1}	$Q_{UV1/2}$. kJ L^{-1}	R^2	k_{QUV}. L kJ^{-1}	$Q_{UV1/2}$. kJ L^{-1}	R^2
Photolysis	0.043	16.008	0.98	0.027	25.672	0.97
Photolysis // SO_4^{2-}	0.05	13.863	0.99	0.027	25.961	0.96
ZnO	0.053	13.203	0.87	0.026	26.355	0.93
ZnO // SO_4^{2-}	0.055	12.534	0.93	0.028	24.58	0.94
TiO_2	0.249	4.652	1	0.026	26.66	0.96
TiO_2 // SO_4^{2-}	0.052	13.33	0.96	0.027	25.672	0.97

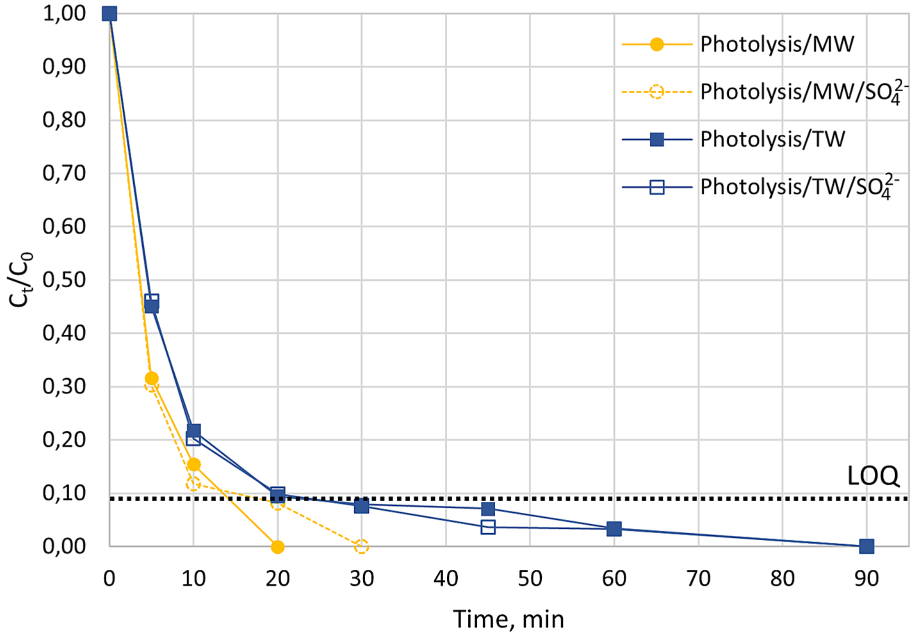


Figure 2. Removal of CIP from MW and TW, by solar-driven photolysis without and in the presence of SO_4^{2-}. Values below LOQ are estimates

this research, 1 gL^{-1} of TiO_2 was immobilized on a glass plate. XRD and SEM indicated that the TiO_2 immobilized on the glass plate was highly pure and uniform in size (39.2–74.9 nm, Triquet et al., 2020]. Many researches claim, that the pH might play an important role for the elimination mechanism of the pharmaceuticals from environmental matrices and modifying the pH leads to structural changes that could enhance or hamper the CIP degradation by direct photolysis via UV radiation. Moreover, it is claimed that FQ removal is very efficient at approx. 7 pH, like this study shows [Sturini et al., 2012, Salma et al., 2016].

Photocatalytic degradation of CIP

The removal efficiency of CIP in the photocatalysis was a much more efficient -compared to the results which were obtained during CIP

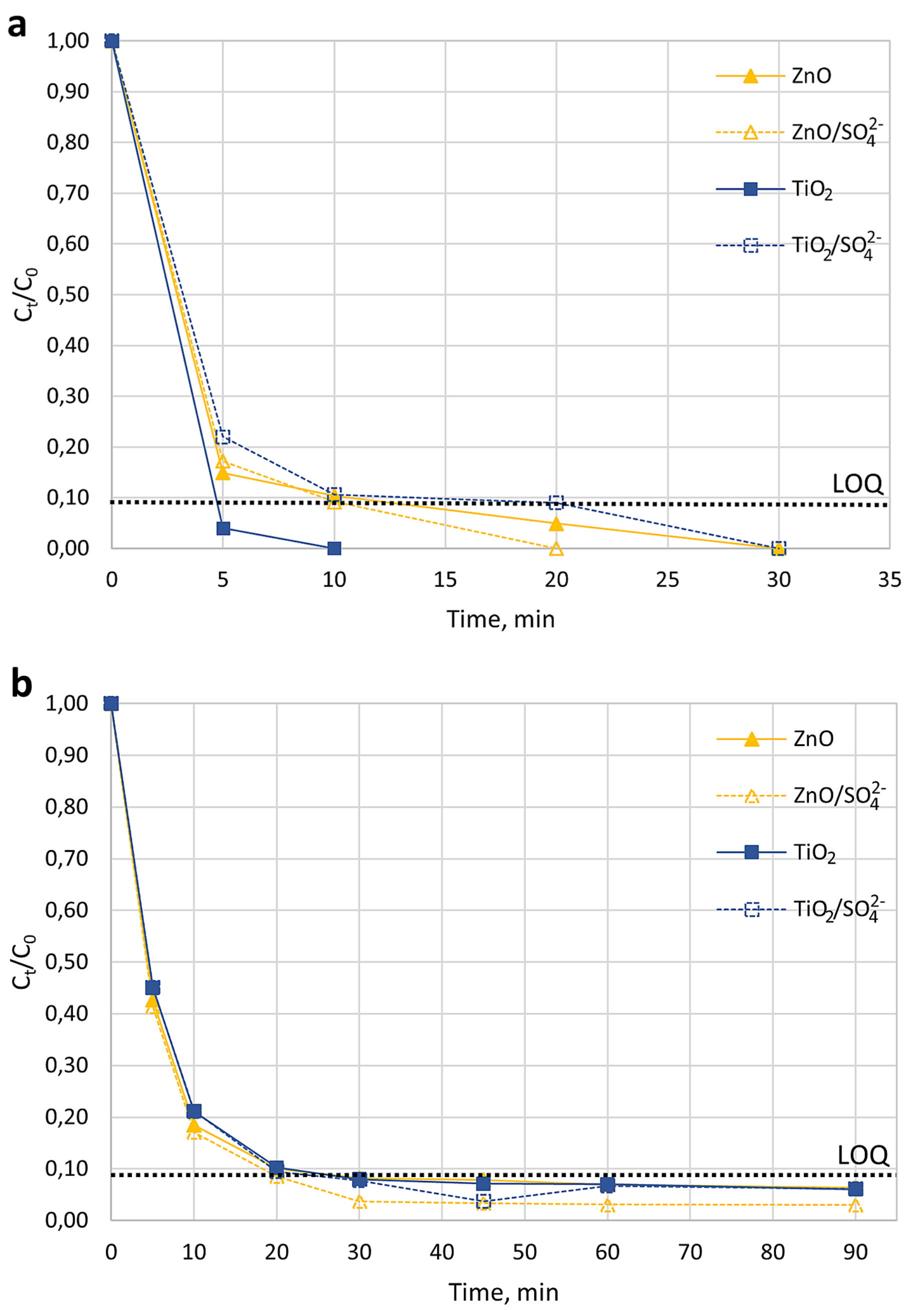


Figure 3. (a) Removal of CIP from MW by solar-driven heterogeneous photocatalysis using TiO2-P25 and ZnO, without and in the presence of SO_4^{2-}. Values below LOQ are estimates; (b) removal of CIP from TW by solar-driven heterogeneous photocatalysis using TiO_2-P25 and ZnO, without and in the presence of SO_4^{2-}. Values below LOQ are estimates

photolysis process. Removal of CIP from MW by heterogeneous TiO_2-P25-based and ZnO-based photocatalysis was 99% and 90% after 5 and 10 minutes, respectively (Figure 3A). The most efficient process was photocatalysis in DW with TiO_2 (Q_{UV} = 21.6 kJ L^{-1}), where photodegradation rate constant estimated k_t = 0.644 min^{-1} and k_{QUV} = 0.249 L kJ^{-1} (Table 3). Solar-driven photocatalysis using ZnO was less efficient process compared to TiO_2-based photocatalysis. The photodegradation rate constants equalled to k_t = 0.227 min^{-1} and k_{QUV} = 0.053 L kJ^{-1}. The presence of sulfates ions alters the dynamic, resulting in a higher efficiency of ZnO-based photocatalysis compared to the degradation with TiO_2 and SO_4^{2-}. The photodegradation rate constants were k_t = 0.24 min^{-1}, k_{QUV} = 0.055 L kJ^{-1} and k_t = 0.225 min^{-1}, k_{QUV} = 0.052 L kJ^{-1}, for ZnO and TiO_2 respectively.

In the case of experiments conducted in TW, the degradation efficiency was significantly lower than in MW. The degradation rates of CIP from TW are comparable for ZnO and TiO_2-based photocatalysis (Figure 3B). However, the efficiency was marginally higher using ZnO, and the photodegradation constants were equalled to k_t = 0.114 min^{-1}, k_{QUV} = 0.026 L kJ^{-1} (Table 3). The presence of SO_4^{2-} in TW slightly increased the efficiency of the photodegradation process, with degradation constants estimated k_t = 0.122 min^{-1}, k_{QUV} = 0.028 L kJ^{-1} and k_t = 0.117 min^{-1}, k_{QUV} = 0.027 L kJ^{-1} for ZnO and TiO_2, respectively. It is suspected that after the process, CIP has been completely removed. However, LOQ = 0.2 mg L^{-1}, which corresponds to a removal rate of over 90%. All values below the LOQ and the CIP degradation efficiencies obtained on their basis are estimates and should be treated as such, because an analytical signal from CIP was still observed in the chromatograms, however it was a signal below the LOQ of the analytical method used.

The TOC analysis results for photocatalysis show the slight decrease of TOC values after the process conducted in MW and in TW. The presence of SO_4^{2-} increased the TOC content in all cases with the exception of ZnO-based photocatalysis. Based on this, it can be stated that the mineralization of CIP does not occur despite the high efficiency of the photocatalytic process. CIP is likely transforming into byproduct(s).

Photocatalysis has been considered as one of the effective and promising technology for the antibiotics residues elimination from water. Compering the efficiency achieved in this study to others results, obtained results are promising. Akter et al. [2022] received the same results, but after 600 minutes of photocatalysis in distilled water (DW) using higher dosage of TiO_2 (0.7 g L^{-1}) and higher concentration of CIP (80 mg L^{-1}). In turn A & Narayanan [2023] achieved a 48% removal after 60 minutes of conducting photocatalysis using bare ZnO (photocatalysts dosage = 200 mg L^{-1} and CIP concentration = 25 mg L^{-1}). The efficiency of photocatalysis is influenced by the complexity of the matrix (presence of inorganic ions) and the type of photocatalyst. Trawiński et al. [2022] proved effect of more complex matrix on the removal efficiency during TiO_2-based photocatalysis. Moreover, Zheng et al. [2023] obtained opposite results for photodegradation of CIP from DW using ZnO and TiO_2, because ZnO occur as more efficient one. On the other hand Gupta et al. [2021] proved that the presence of SO_4^{2-} ions caused negligible adverse effect on photodegradation efficiency, despite much more researches show opposite trend [Chládková et al., 2015; Chen et al., 2017].

CONCLUSIONS

During the tests, control studies carried out in dark conditions showed that in the subsequent minutes of the process the equilibrium of the process is not clearly established – successive phenomena of sorption and desorption of CIP from the photocatalyst surface can be observed, but these values never exceed the values 33% percent like in experiment conducted in MW with TiO_2. It can therefore be assumed that any CIP removal in studies using light that exceeds this value will be related to the actual decomposition of the CIP molecule. Solar-driven photocatalysis using TiO_2-P25 and ZnO improved the removal efficiency of CIP compared to its solar photolysis. Its efficacy is effected by the matrix complexity, presence of inorganic ions, and the type of used photocatalyst. ZnO-based photocatalysis occurs more efficient in a more complex matrix, although TiO_2 demonstrated higher efficiency in degrading CIP in MW in the presence of SO_4^{2-}. The presence of SO_4^{2-} in DW hinders the photodegradation of CIP, whereas in TW, it accelerates the process. However, despite the high efficiency in photodegradation of CIP molecules, its mineralization resulting in TOC concentration decreasing was not observed.

Further research should include: experiments in environmental matrices; tests with other anions such as chlorides, carbonates and nitrates - which may act as radical scavengers; and natural sources of irradiation. Additionally, it is necessary to examine whether the by-products formed during the processes do not exhibit greater ecotoxicity than the parent compound. Finding a method for the mineralization of this kind micropollutant is also imperative.

Acknowledgments

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