

# Photocatalytic degradation of pharmaceuticals present in conventional treated wastewater by nanoparticle suspensions



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## ABSTRACT

Pharmaceuticals have become an important public health issue as environmental pollutants over the last years. After ingestion, pharmaceuticals are partly excreted unchanged. They can reach the wastewater treatment plant (WWTP) via the sewer network. Because the conventional treatments are ineffective in their removal, new methods should be approached, for example semiconductor photocatalysis. Several of the hitherto published studies analyzed the degradation of model pollutants but for the degradation of pharmaceuticals in unspiked real wastewater further investigations are required. Therefore, we want to focus on the removal of pharmaceuticals in an actual effluent from a WWTP and investigate the effluent background effect. This study shows the heterogeneous photocatalytic degradation of 14 pharmaceuticals with initial concentrations  $C_i > 0.3 \mu\text{g L}^{-1}$  present in a WWTP effluent. We found that UVA ( $1.5 \text{ mW cm}^{-2}$ , intensity peak at 365 nm) irradiation of  $\text{TiO}_2$  P25 ( $A_s = 56 \text{ m}^2 \text{ g}^{-1}$ ) or ZnO ( $A_s = 5.23 \text{ m}^2 \text{ g}^{-1}$ ) nanoparticles leads to considerable degradation of the analyzed pharmaceuticals. With ZnO nanoparticles, 40 min UVA irradiation was sufficient to degrade over 95% of these pharmaceuticals ( $k_{\text{app}} = 8.6 \times 10^{-2} \text{ s}^{-1}$ ). Using  $\text{TiO}_2$  P25 on the other hand, it would take more than six times longer to reach the same level ( $k_{\text{app}} = 1.4 \times 10^{-2} \text{ s}^{-1}$ ). Carbamazepine dissolved in millipore water served as a comparison model. Also in this system ZnO presents faster degradation.

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## 1. Introduction

Pharmaceuticals emerging in the aquatic ecosystems have become an important public health issue over the past few years. To evaluate the impact of those pharmaceuticals in drinking water the World Health Organization already reviewed scientific evidence to address this issue. They are mostly introduced in the sewage system through excretion of unmetabolized compounds after medical use or inappropriate disposal [1–4] and then transported into the wastewater treatment plants (WWTPs). However, conventional WWTPs are not designed to treat water polluted with pharmaceuticals present at trace levels and therefore, the applied treatments are ineffective in their removal

[5,6]. Consequently, they reach the aquatic system and can be found in surface and ground water [7,8], soil and sediments [8,9] and even in drinking [10,11] and tap water [8,12]. Although, normally pharmaceuticals do not present acute toxic effects on aquatic organisms due to their low concentrations, in the range of ng to  $\mu\text{g}$  per liter, concerns have been raised for chronic exposure, due to their continuous input into the environment, acting as slightly persistent pollutants [2,4,13].

For these reasons, diverse efforts have been made to remove pharmaceuticals from wastewater, such as membrane filtration, activated carbon adsorption and advanced oxidation processes (AOPs). AOPs are recommended when water pollutants have a high chemical stability, allowing to achieve almost the total mineralization of contaminants to carbon dioxide, water and inorganic compounds or, at least, allow their partial oxidation to become more biodegradable and/or less harmful [3,14].

Different techniques involve the generation of hydroxyl radicals, which are nonselective and have twice the oxidizing

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**Table 1**  
Drugs (LLOQ – lower limit of quantification).

Analyte	Drug class	Provider	Internal standard	LLOQ
Carbamazepine	Anticonvulsant	Sigma	Carbamazepine D10	50 ng L <sup>-1</sup>
Gabapentin		Pfizer	Gabapentin D10	200 ng L <sup>-1</sup>
Lamotrigine		Sigma	Lamotrigine 13C, 15N4	50 ng L <sup>-1</sup>
Oxcarbazepine		Cerilliant	Carbamazepine D10	50 ng L <sup>-1</sup>
Venlafaxine	Antidepressant	Wyeth	Venlafaxine D6	50 ng L <sup>-1</sup>
Bisoprolol	Beta blocker	Merck	Oxprenolol	50 ng L <sup>-1</sup>
Celiprolol		LGC Standards	Oxprenolol	50 ng L <sup>-1</sup>
Talinolol		LGC Standards	Venlafaxine D6	50 ng L <sup>-1</sup>
Bezafibrate	Lipid-lowering drug	Sigma	Warfarin	50 ng L <sup>-1</sup>
Tramadol	Opioid analgesic	Sigma	Tramadol 13C, D3	50 ng L <sup>-1</sup>
Candesartan	Angiotensin receptor antagonist	AstraZeneca	Amitriptyline D3	50 ng L <sup>-1</sup>
Eprosartan		Sigma	Venlafaxine D6	50 ng L <sup>-1</sup>
Irbesartan		Sigma	Trimipramine D3	50 ng L <sup>-1</sup>
Valsartan		Sigma	Valsartan D9	100 ng L <sup>-1</sup>

power of chlorine [4,6,15–17]. Heterogeneous semiconductor photocatalysis has become an attractive method to remediate environmental contamination due to its high photocatalytic activity, non-toxicity and photostability [3,15,18–21]. However, most of the studies do not use unspiked wastewater from sewage treatment plants but aqueous solutions of model compounds or surface waters. Therefore, we want to degrade pharmaceuticals in effluent samples from a WWTP and investigate the effluent background effect. To do so, we additionally investigated the degradation process in millipore water artificially spiked with carbamazepine.

As photocatalysts we chose TiO<sub>2</sub> and ZnO and compared the degradation efficiencies of both photocatalysts. Despite several semiconductors have been studied for applications in wastewater decontamination, ZnO and TiO<sub>2</sub> are frequently the most studied photocatalysts because of their interesting optical properties, low cost, and availability [22]. Although ZnO is usually described as the most active semiconductor [23], TiO<sub>2</sub> is used more frequently because it is more stable than ZnO in aqueous solution [24]. We used the photocatalysts as nanoparticles in a slurry mixture to maximise the surface area of the system. The upscaling of such a setup provides a challenge regarding the separation of the nanoparticles from water after the treatment. In the light of an active research regarding this problem, we think that this can be solved in the near future, for example through the use of magnetic core nanoparticles [25,26]. Whenever photocatalytic systems are applied in an actual wastewater treatment plant, a risk assessment regarding the material output into the environment is necessary, due to their photo activity, size distribution and potential toxicity for aquatic organisms in the case of ZnO [27].

## 2. Experimental part

### 2.1. Chemicals and materials

For the degradation experiments, TiO<sub>2</sub> P25 (kindly provided by Evonik), ZnO (IOLITEC Ionic Liquids Technologies GmbH), and carbamazepine (Sigma Aldrich) were used in this work. Water was obtained from a Millipore Milli-Q System (Water, Millipore). For the SPE-HPLC-MS/MS analysis, acetonitrile, methanol (HiperSolv, HPLC-grade), and ammonium acetate were purchased from Merck. Formic acid (LC-MS grade) and Na<sub>2</sub>EDTA (ACS reagents) were obtained from Sigma and water (HPLC-grade) from VWR. The standards were provided by different suppliers as listed in Table 1. The treated wastewater was kindly provided by the WWTP Kaditz located in Dresden, Germany, operated by

Stadtentwässerung Dresden GmbH. This treatment plant currently cleans the sewage of 650,000 people and has a design capacity of 740,000 inhabitant equivalents. The yearly average sewage volume is about 55 × 10<sup>6</sup> m<sup>3</sup>. The WWTP consist of primary clarifier, activated sludge reactor and secondary clarifier [28]. The sample was taken as a 24 h flow proportional composite effluent sample on June 24th 2014, stored at 4 °C and analyzed on the next day. Further characteristics of the sewage sample are summarized in Table 2.

### 2.2. Nanoparticle characterization

The specific surface area of the photocatalyst particles was determined by the Brunauer–Emmett–Teller (BET) method. This property was analyzed at 77 K by nitrogen adsorption–desorption in a Micromeritics TriStar analyzer (Micromeritics). Before performing adsorption experiments, samples (0.5 g) were out-gassed at 26.7 Pa and 350 °C for 6 h.

The morphology for both particle types were analyzed with a scanning electron microscope (SEM) operated at 10 kV and 25 kV.

The UV–vis diffuse reflectance spectra were obtained using a Shimadzu UV–vis spectrophotometer 2101PC in the range of 190–600 nm. It was equipped with a diffuse reflectance attachment and we used BaSO<sub>4</sub> as a reference.

### 2.3. Photocatalytic degradation experiments

The photocatalytic degradation was carried out in borosilicate beakers (VWR) with 3.3 mm wall thickness and 5 cm diameter. Under constant stirring 1 g L<sup>-1</sup> of TiO<sub>2</sub> P25 or ZnO was added to the

**Table 2**  
Treated wastewater parameters.

COD (chemical oxygen demand)	37 mg L <sup>-1</sup>
BOD (biochemical oxygen demand)	4 mg L <sup>-1</sup>
Nitrogen	
N <sub>total</sub>	12.0 mg L <sup>-1</sup>
TKN (total Kjeldahl nitrogen)	<5.0 mg L <sup>-1</sup>
N <sub>ammonium</sub>	0.31 mg L <sup>-1</sup>
N <sub>nitrite</sub>	0.03 mg L <sup>-1</sup>
N <sub>nitrate</sub>	7.40 mg L <sup>-1</sup>
N <sub>inorganic</sub>	7.74 mg L <sup>-1</sup>
Phosphor	
P <sub>total</sub>	0.86 mg L <sup>-1</sup>
P <sub>phosphate</sub>	0.56 mg L <sup>-1</sup>
pH	7.5

samples. Prior to illumination, the solutions containing the catalyst were stirred in the dark for 30 min to achieve an adsorption–desorption equilibrium of the pharmaceuticals on the photocatalyst surface. Afterwards, the samples were exposed to UVA-radiation. The illuminating device (UMEX) was equipped with six Philips 8 W mercury fluorescent tubes ( $E_{\max}$  at 365 nm).

The distance between the energy source and the photocatalytic reactor was 15 cm. At this position the UVA intensity was determined by an UV34 Lux Meter (PCE) ranging from 1.5 to 1.6 mW cm<sup>-2</sup>. Aliquots of 2 mL of the reaction solution were withdrawn at determined time intervals and centrifuged for 1 h to remove the catalyst nanoparticles. All experiments were carried out at room temperature. As controls, experiments were carried out in the absence of catalyst nanoparticles or without UVA irradiation. All other parameters in the control experiments were kept unchanged.

The effluent sample from the WWTP Kaditz was filtered by a filter paper (VWR pore sizes 5–13 μm) to remove suspended particulate matter. Thereafter, 1 g L<sup>-1</sup> of catalyst was added to a volume of 100 mL of the treated wastewater. The suspension was then exposed under continuous stirring to UVA-radiation. Afterwards, the samples were centrifuged and analyzed by the SPE-HPLC–MS/MS method.

In contrast to the previous experiment, we artificially spiked millipore water with carbamazepine. Therefore, 50 mL of 12 mg L<sup>-1</sup> carbamazepine solution with 1 g L<sup>-1</sup> of catalyst was exposed under continuous stirring to UVA-radiation. The samples were filtered (Rotilabo nylon, pore size 0.2 μm) and centrifuged. Absorbance measurements were performed with a Varian CARY-100 UV-VIS Spectrophotometer. The quantification limit for carbamazepine in this setup is 300 μg L<sup>-1</sup>.

#### 2.4. Analytic method

The analysis of the WWTP effluent sample and the degradation experiments were conducted with a SPE-HPLC–MS/MS-method, which has been described in the work of Gurke et al. [29]. Briefly summarized, 1 mL of the degradation experiment sample was taken, adjusted to a pH of 3 by using formic acid and spiked with 100 μL of the Internal Standard (IS) solution (10 μg L<sup>-1</sup>). The samples were extracted using an Abimed ASPEC XL (Gilson) with Oasis HLB 10 mg Extraction Cartridges (Waters). The eluates were evaporated to dryness under a gentle air stream at 50 °C and re-dissolved in 250 μL mixture of solvent A and solvent B (80/20, v/v). The solvents A (97/3/0.05; v/v/v) and B (5/95/0.05; v/v/v) were a composition of 2 mM ammonium acetate solution, acetonitrile, and formic acid. A LC–MS/MS system, consisting of a Dionex-HPLC composed of an UltiMate3000 Pump and Autosampler (Thermo Fischer Scientific) with a Chromleon 7 Chromatography Data System (Dionex Softron) and coupled to an API 4000 tandem mass spectrometer (AB Sciex) equipped with an electrospray ionization source (ESI), was used for the analyses of the samples. The chromatographic separation was performed with a Synergi 2.5u HydroRP 100A, 100 mm × 2.0 mm and a C18 security guard 4 mm × 2 mm (both Phenomenex) using a multi step gradient out of solvent A and B with a total runtime of 15 min. For the analyses, an injection volume of 20 μL was chosen. The mass spectrometric analyses were performed in multiple reaction monitoring (MRM) mode with positive electrospray ionization. The Analyst data system 1.6 (AB Sciex) was applied for MS control and for the peak area evaluation, regression analysis of calibration curves and calculation of concentrations.

#### 2.5. Photocatalytic degradation model

To study the photocatalytic oxidation process we used a suspension of photocatalytic nanoparticles due to the large specific

surface area in such a system. Additionally, it is possible to model the degradation process in this case efficiently as shown by [30]. The simplified reaction formula to describe the degradation process is



where  $A(\text{aq})$  is the investigated organic molecule in solution and  $A(\text{ad})$  represents the adsorbed molecule.  $M(\text{aq})$  represents the mineralized components that are formed during the reaction. Temporal changes of the molecule concentration in the solution  $C_{A(\text{aq})}$  (in 1 m<sup>-3</sup>) and the concentration on the photocatalyst particle surface  $C_{A(\text{ad})}$  (in 1 m<sup>-2</sup>) are given by

$$\frac{d}{dt} C_{A(\text{ad})} = j_{\text{ads}} - j_{\text{des}} - j_{\text{reac}} \quad (2)$$

$$\frac{d}{dt} C_{A(\text{aq})} = a_s (j_{\text{des}} - j_{\text{ads}}) \quad (3)$$

These equations include the specific surface area of the nanoparticles  $a_s$  (surface area per solution volume) and different molecule fluxes

$$j_{\text{ads}} = k_{\text{ads}} (1 - \Theta) C_{A(\text{aq})} \quad (4)$$

$$j_{\text{des}} = k_{\text{des}} C_{A(\text{ad})} \quad (5)$$

$$j_{\text{reac}} = k_{\text{reac}} C_{A(\text{ad})} \quad (6)$$

These molecule fluxes are mainly determined by the corresponding concentrations and the three different rate constants, describing the reaction ( $k_{\text{reac}}$ ), adsorption ( $k_{\text{ads}}$ ) and desorption ( $k_{\text{des}}$ ) processes. For the adsorption process is also the surface coverage important ( $\Theta$ ).

In the present case of a fast establishing adsorption–desorption equilibrium with quasi-stationary surface concentration  $C_{A(\text{ad})} = 0$  (i.e.  $|C_{A(\text{ad})}| \ll k_{\text{ads}} C_{A(\text{aq})}$ ,  $k_{\text{des}} C_{A(\text{ad})}$ ), the surface concentration in the system of Eqs. (2) and (3) can be eliminated. The solution of Eq. (2) in the limit of small coverage  $\Theta \ll 1$  reads  $C_{A(\text{ad})} = C_{A(\text{aq})} k_{\text{ads}} (k_{\text{des}} + k_{\text{reac}})^{-1}$ . Insertion of this expression into Eq. (3) yields  $C_{A(\text{aq})} = -k_{\text{app}} C_{A(\text{aq})}$  with the solution

$$C_{A(\text{aq})}(t) = C_{A(\text{aq}),0} \exp(-k_{\text{app}} t) \quad (7)$$

where the apparent degradation rate constant is given by

$$k_{\text{app}} = a_s k_{\text{ads}} k_{\text{reac}} (k_{\text{des}} + k_{\text{reac}})^{-1} \quad (8)$$

Thus, for  $k_{\text{des}} \ll k_{\text{reac}}$ , we find  $k_{\text{app}} = a_s k_{\text{ads}}$ . This means that the degradation rate becomes adsorption-limited and does not depend on the reaction rate constant.

### 3. Results and discussion

#### 3.1. Characterization of TiO<sub>2</sub> and ZnO nanoparticles

A specific surface area of 56 m<sup>2</sup> g<sup>-1</sup> was obtained for the TiO<sub>2</sub> P25 nanopowder with the BET method. For the ZnO nanopowder a specific surface area of 5.23 m<sup>2</sup> g<sup>-1</sup> was found. In suspension it is expected an additional clustering, especially for TiO<sub>2</sub>, which will reduce the active surface area.

This difference can also be qualitatively observed in the SEM images (Fig. 1). TiO<sub>2</sub> particles show a finer structure than the ones in the ZnO sample. TiO<sub>2</sub> is present as monodisperse nanospheres. In the ZnO powder more complex polydisperse rectangular structures were found.

The UV–vis diffuse reflectance spectra of ZnO and TiO<sub>2</sub> are included in Fig. 2. Also the emission spectra of the radiation lamp is plotted in the figure. It can be observed that ZnO absorbance

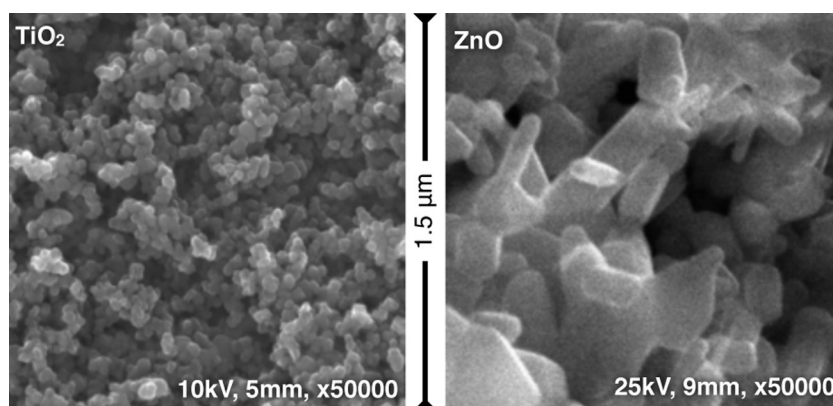


Fig. 1. SEM images of colloidal TiO<sub>2</sub> and ZnO.

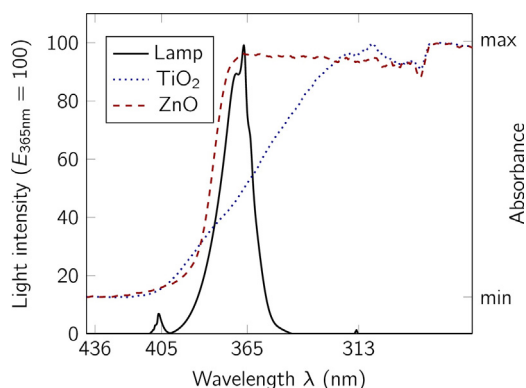


Fig. 2. Light output of the used mercury fluorescent tubes normalized at 365 nm compared to the diffuse reflectance spectra of TiO<sub>2</sub> and ZnO.

already reached its highest level at 365 nm. In contrast, the absorption potential of TiO<sub>2</sub> reaches its maxima around 310 nm. This indicates that with ZnO the light source can be utilized more efficiently.

### 3.2. Influence of WWTP effluent

Carbamazepine's photodegradation was evaluated in a real WWTP effluent sample, alongside other occurring pharmaceuticals as listed in Table 1. The effluent of a WWTP represents a challenging matrix for photocatalytic degradation. Different parameters like ion concentration, pH value or the manifold mixture of organic and inorganic molecules lead us to conjecture about the concentration development over time that may be altered compared to a 'clean' laboratory experiment. To examine this assumption we selected the anticonvulsant carbamazepine dissolved in millipore water, as a comparison 'clean' degradation experiment.

To assure that only the combination of nanoparticles and UV-radiation causes the degradation of the pharmaceuticals, two different control experiments were conducted without nanoparticles and without UVA irradiation for 45 min. In the case of the control exposed to UVA-radiation no significant change in the monitored concentrations occurred. After irradiation the average change over all monitored drugs was 0.8% (SD 4.8%). However for the controls with nanoparticles kept in the dark we observed an initial drop of the concentrations before they stabilized, so that the changes in concentration after the initial 30 min of adsorption is 0.3% (SD 4.9%) for TiO<sub>2</sub> and 0.2% (SD 5.7%) for ZnO. This effect is due to the adsorption on the catalyst's surface until the adsorption-desorption equilibrium is reached. This is consistent with the idea

that the UVA-radiation *per se* does not induce the degradation process nor the nanoparticles without UVA irradiation.

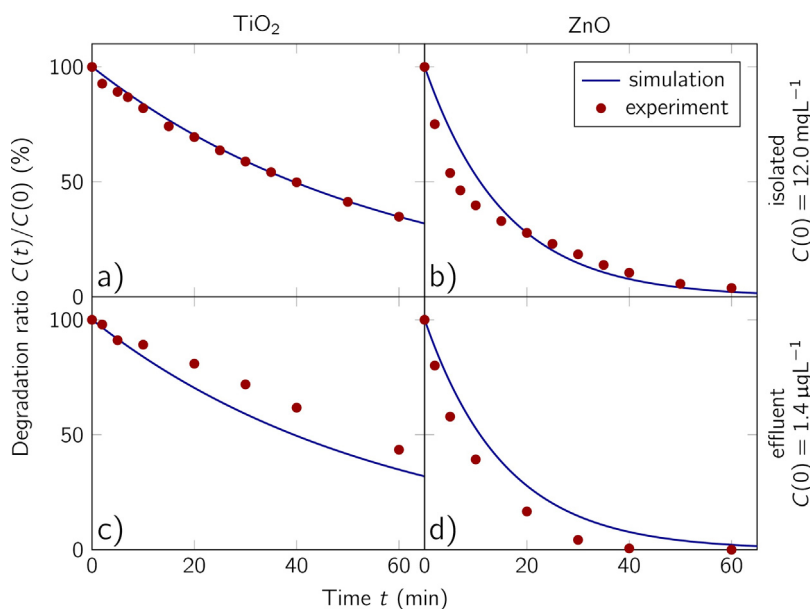
Carbamazepine's concentration was considerably reduced over time in the presence of the catalysts and UVA-radiation. The same behaviour was observed for carbamazepine present in the wastewater effluent sample. In Fig. 3 we compare the four experiments with carbamazepine dissolved in millipore water and present in the effluent. It can be noticed that the degradation by ZnO is significantly faster than with TiO<sub>2</sub> in both setups which is in high accordance with the conducted simulation of the degradation. These results are shown in Table 3 and demonstrate that carbamazepine can adsorb more than 40 times faster on the ZnO than on the TiO<sub>2</sub> surface. Because of this, ZnO presents a higher degradation rate compared to TiO<sub>2</sub> regardless its larger surface area.

When the parameters determined from the millipore water experiment (Fig. 3a and b) are compared to the outcome from the effluent (Fig. 3c and d) similar results can be found. This shows that the effluent background does not reduce the efficiency of the selected photocatalytic particles, and the method to model the degradation in the millipore water experiment can also be applied for pharmaceuticals investigated in the effluent.

### 3.3. Degradation of pharmaceuticals in the WWTP effluent

To determine the degradation in an effluent sample of the WWTP Dresden Kaditz, 55 target pharmaceuticals based on their prescription numbers were selected based on a previous study of Gurke et al. [29]. For monitoring the degradation process, the initial concentration ( $C_i$ ) of the pharmaceuticals needs to be significantly higher than the corresponding detection limit. Therefore, we set the lower limit to be  $C_i > 0.3 \mu\text{g L}^{-1}$ . After an initial analysis of the effluent sample, 14 pharmaceuticals were selected to be monitored in the degradation experiment (Table 1).

Based on this criteria the anticonvulsants carbamazepine ( $C_i = 1.29 \mu\text{g L}^{-1}$ ), gabapentin ( $C_i = 11.30 \mu\text{g L}^{-1}$ ), lamotrigine ( $C_i = 0.98 \mu\text{g L}^{-1}$ ), and oxcarbazepine ( $C_i = 0.63 \mu\text{g L}^{-1}$ ), the antidepressant venlafaxine ( $C_i = 0.58 \mu\text{g L}^{-1}$ ), the beta blockers bisoprolol ( $C_i = 0.58 \mu\text{g L}^{-1}$ ), celiprolol ( $C_i = 0.35 \mu\text{g L}^{-1}$ ), and talinolol ( $C_i = 0.43 \mu\text{g L}^{-1}$ ), the lipid-lowering drug bezafibrate ( $C_i = 0.48 \mu\text{g L}^{-1}$ ), the opioid analgesic tramadol ( $C_i = 0.624 \mu\text{g L}^{-1}$ ), as well as the angiotensin receptor antagonists candesartan ( $C_i = 1.30 \mu\text{g L}^{-1}$ ), eprosartan ( $C_i = 0.56 \mu\text{g L}^{-1}$ ), irbesartan ( $C_i = 1.50 \mu\text{g L}^{-1}$ ), and valsartan ( $C_i = 3.59 \mu\text{g L}^{-1}$ ) were analysed in the degradation experiment. Please keep in mind that this data is a mere snapshot because the concentration of micropollutants can significantly vary in sewage samples based on a diverse range of parameters, like weather conditions.



**Fig. 3.** Measured concentration during the degradation of carbamazepine under UVA irradiation with  $1 \text{ g L}^{-1}$  catalysts  $\text{TiO}_2$  (a + c) and  $\text{ZnO}$  (b + d). In the upper row, carbamazepine was dissolved in millipore water (a + b) and measured by UV/VIS spectrophotometry. In the lower row the results of the degradation of carbamazepine in the treated effluent analysed by HPLC–MS/MS-method are shown. The full lines represent fits for carbamazepine dissolved in millipore water according to the presented model using the values of  $k_{\text{ads}}$  and  $k_{\text{des}}$  determined from experiments in the dark (Table 3).

**Table 3**

Adsorption and desorption rate constants derived from the experiments with carbamazepine using photocatalytic  $\text{TiO}_2$  and  $\text{ZnO}$  nanoparticles.

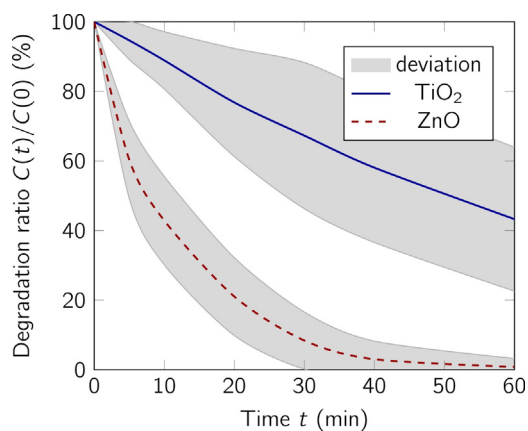
Catalysts	$k_{\text{ads}}$ ( $\text{ms}^{-1}$ )	$k_{\text{des}}$ ( $\text{s}^{-1}$ )
$\text{TiO}_2$	$5.3 \times 10^{-9}$	$4.5 \times 10^{-4}$
$\text{ZnO}$	$2.2 \times 10^{-7}$	$5.9 \times 10^{-3}$

**Table 4**

Apparent rate constants average and adsorption rate constants average for the 14 studied pharmaceuticals (Table 1) with the photocatalysts  $\text{TiO}_2$  and  $\text{ZnO}$ .

Catalyst	$k_{\text{app}}$ ( $\text{s}^{-1}$ )	$k_{\text{ads}}$ ( $\text{ms}^{-1}$ )
$\text{TiO}_2$	$1.4 \times 10^{-2}$	$4.0 \times 10^{-9}$
$\text{ZnO}$	$8.6 \times 10^{-2}$	$2.7 \times 10^{-7}$

The degradation experiments were traced for all target pharmaceuticals and are presented in the [supplementary material](#). For the SPE extraction just a small sample volume of 1 mL was necessary, which allowed a high temporal resolution monitoring (ten samples in 1 h) without disturbing the experiment by taking out samples with a large volume. An overview of the two photocatalytic materials is shown in Fig. 4. After 40 min, an average degradation of more than 95% for the samples treated with  $\text{ZnO}$  was already observed. During the same period of time the pharmaceuticals treated with  $\text{TiO}_2$  degraded by 40%. The simulation data shows that treatment with  $\text{TiO}_2$  would take over 4 h to



**Fig. 4.** Average degradation ratio over time of the 14 selected pharmaceuticals (Table 1) measured by HPLC–MS/MS-method. The grey area corresponds to the standard deviation.

achieve the same result as  $\text{ZnO}$ . These differences in degradation rates are even more significant taking into account the smaller surface area of  $\text{ZnO}$ . The resulting apparent rate constants and adsorption rate constants are listed in Table 4 and are in accordance with the results from carbamazepine dissolved in millipore water. In literature different new approaches besides commercial nanoparticles are presented. The apparent rate constants found for example from  $\text{TiO}_2$  nanowires is in average the same order of magnitude as the commercial  $\text{TiO}_2$  particles, but slower compared to the  $\text{ZnO}$  particles [31]. Furthermore, it was observed a lower selectivity of  $\text{ZnO}$  compared to  $\text{TiO}_2$ . In the  $\text{ZnO}$  experiments, all target pharmaceuticals are degraded in a similar way with just slight deviations. This characteristic is very important in real applications due to the different mixtures of pharmaceuticals present in wastewater depending on regional consumption patterns or season of the year. It can be assumed that the treatment of pharmaceuticals present in WWTP effluents using  $\text{ZnO}$  and UVA-radiation will result in a near complete degradation of the pollutants in a relative short period of time.

#### 4. Conclusions

In general, pharmaceuticals are not fully removed by urban WWTPs and can be detected in the effluents. Removing these type of pollutants from wastewater effluents would be useful to prevent the contamination of surface water. Semiconductor photocatalysis is recommended whenever water pollutants present low degradability and/or high chemical stability.

The pollutants are at least in parts mineralized due to the generation of highly oxidative species and electron-hole pairs. Photocatalysis may be seen as a complementary method to the

already existing technologies to improve the removal rates of pollutants, such as pharmaceuticals. In this study, the applicability of a previously developed LC–MS/MS method by evaluating the degradation of pharmaceuticals present in a real wastewater sample by photocatalysis has been demonstrated. We were able to conduct successfully degradation experiments of various pharmaceuticals present in the effluent of a WWTP via photocatalysis by ZnO and TiO<sub>2</sub> under UVA-radiation. Although ZnO shows higher degradation rates it poses a strong engineering challenge, to prevent ZnO contamination of the aquatic environment, due to its potential toxicity.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jece.2015.10.045>.

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