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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 $C_i > 0.3\ \mu g\ L^{-1}$ present in a WWTP effluent. We found that UVA ($1.5\ mW\ cm^{-2}$, intensity peak at 365 nm) irradiation of TiO_2 P25 ($A_s = 56\ m^2\ g^{-1}$) or ZnO ($A_s = 5.23\ m^2\ g^{-1}$) 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 ($k_{app} = 8.6 \times 10^{-2}\ s^{-1}$). Using TiO_2 P25 on the other hand, it would take more than six times longer to reach the same level ($k_{app} = 1.4 \times 10^{-2}\ s^{-1}$). Carbamazepine dissolved in millipore water served as a comparison model. Also in this system ZnO presents faster degradation.

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 μg 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^{-1}
Gabapentin		Pfizer	Gabapentin D10	200 ng L^{-1}
Lamotrigine		Sigma	Lamotrigine 13C, 15N4	50 ng L^{-1}
Oxcarbazepine		Cerilliant	Carbamazepine D10	50 ng L^{-1}
Venlafaxine	Antidepressant	Wyeth	Venlafaxine D6	50 ng L^{-1}
Bisoprolol	Beta blocker	Merck	Oxprenolol	50 ng L^{-1}
Celiprolol		LGC Standards	Oxprenolol	50 ng L^{-1}
Talinolol		LGC Standards	Venlafaxine D6	50 ng L^{-1}
Bezafibrate	Lipid-lowering drug	Sigma	Warfarin	50 ng L^{-1}
Tramadol	Opioid analgesic	Sigma	Tramadol 13C, D3	50 ng L^{-1}
Candesartan	Angiotensin receptor antagonist	AstraZeneca	Amitriptyline D3	50 ng L^{-1}
Eprosartan		Sigma	Venlafaxine D6	50 ng L^{-1}
Irbesartan		Sigma	Trimipramine D3	50 ng L^{-1}
Valsartan		Sigma	Valsartan D9	100 ng L^{-1}

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_2 and ZnO and compared the degradation efficiencies of both photocatalysts. Despite several semiconductors have been studied for applications in wastewater decontamination, ZnO and TiO_2 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_2 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_2 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_2EDTA (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 55×10^6 m^3. 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 outgassed 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 $BaSO_4$ 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^{-1} of TiO_2 P25 or ZnO was added to the

Table 2
Treated wastewater parameters.

COD (chemical oxygen demand)	37 mg L^{-1}
BOD (biochemical oxygen demand)	4 mg L^{-1}
Nitrogen	
N_{total}	12.0 mg L^{-1}
TKN (total Kjeldahl nitrogen)	<5.0 mg L^{-1}
$N_{ammonium}$	0.31 mg L^{-1}
$N_{nitrite}$	0.03 mg L^{-1}
$N_{nitrate}$	7.40 mg L^{-1}
$N_{inorganic}$	7.74 mg L^{-1}
Phosphor	
P_{total}	0.86 mg L^{-1}
$P_{phosphate}$	0.56 mg L^{-1}
pH	7.5