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Removal of selected persistent organic pollutants by heterogeneous photocatalysis in water

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Abstract

Environmentally relevant polar persistent organic pollutants (pharmaceuticals and diagnostic agents) were chosen according to human consumption and occurrence in the aquatic environment (sewage plant effluents, rivers and groundwater) to investigate their behavior during photocatalytic oxidation. From data compilation in the literature, the active metabolite clofibric acid of some lipid lowering agents, the anti-epileptic drug carbamazepine and the X-ray contrast media iomeprol were selected. The degradation of the persistent pollutant was monitored by HPLC/DAD/FLD. The study also focuses on the identification and quantification of possible degradation products by HPLC/DAD/FLD and HPLC/MS/MS. The degradation process was also monitored by determination of sum parameters and inorganic ions. Various aromatic and aliphatic degradation products have been identified and quantified. From analytical data, a possible degradation scheme for carbamazepine was proposed. Kinetic studies showed that the TiO_2 photocatalyst P25 was more active in clofibric acid degradation than Hombikat UV100. For photocatalytic degradation of iomeprol Hombikat UV100 was more suitable than P25. In general the presence of NOM and carbamazepine retarded the photocatalysis of clofibric acid. Radiation attenuation, competition for active sites and surface deactivation of the catalyst by adsorption are the reason for that. The results of this work proof that photocatalysis is a promising technology to reduce persistent substances even if they are present in low concentrations or in a complex matrix.

Keywords: Persistent organic pollutant; Pharmaceuticals; X-ray contrast media; Degradation products; TiO_2; 75% anatase and 25% rutile (P25); 100% anatase (Hombikat UV100); Aqueous suspensions; Water treatment; Competitive inhibition

1. Introduction

Nowadays, the occurrence of polar persistent organic pollutants in the environment, like pharmaceutical and diagnostic media residues, has become a subject of major public interest. In Europe and the U.S., residues of pharmaceutical and diagnostic compounds have been detected in effluents of sewage treatment plants, surface [1–4], ground and drinking waters [5,6]. When applying pharmaceuticals and diagnostic agents to humans, many of their constituents are excreted unchanged through urine and faeces or as metabolites and find their way to the public sewage system, and finally to the receiving waters. For example, the iodinated X-ray contrast media for medical applications are responsible for the high concentrations of organically bound halogens adsorbable on activated carbon (AOX) in hospital wastewater and as a consequence in the effluents of sewage treatment plants. Balances of the input and the output of drugs and diagnostic agents in sewage treatment plants reveal that some of them are by far not removed quantitatively by current techniques [4]. The refractory properties of these substances lead to an unfavorable accumulation in the environment. As both the use and discharge of pharmaceuticals and diagnostic agents into the aquatic environment seem to be difficult to control and impossible to avoid, an effective treatment technology for the removal of these compounds is indispensable. In recent studies, it was demonstrated that among the classical drinking water treatment processes only ozonation and filtration through new granular activated carbon partly eliminated some pharmaceuticals [7]. The potential of UV/H_2O_2 [8,9], O_3/H_2O_2 [9,10] and ozonation [9–11] for partial elimination of pharmaceuticals and contrast media was investigated. In addition, photocatalysis turned out to be a promising tool for water treatment [12,13]. The most widely

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investigated photocatalyst for the degradation of organic pollutants is TiO_2. TiO_2 is remarkably active, cheap, non-toxic and chemically stable over a wide pH range and it is not subject to photo corrosion. In general, the goal of the application of photocatalysis in water treatment is the transformation, deactivation and finally minimization of environmentally persistent compounds or xenobiotics. The aim of this work was to (1) study the photocatalytic degradation of clofibric acid (lipid lowering agent of the applied drugs clofibrate ethyl, etofibrate and ethofyllinclofibrate), carbamazepine (anti-epileptic/analgetic), and iomeprol (iodinated X-ray contrast media) in aqueous TiO_2 suspensions and (2) to assess the potential of two different TiO_2 materials (Hombikat UV100 and P25) for photocatalytic oxidation of the selected aquatic pollutants. The photocatalytic degradation kinetics were examined by variation of the TiO_2 and the initial pollutant concentrations. The main degradation products were identified and quantified. Moreover, the influence of the complex situation in real waste or raw waters in the photocatalysis experiments had to be assessed. The investigations include the influences of organic water constituents like natural organic matter (NOM) from a bog water lake (Lake Hohloh), and of mixtures of competing pharmaceuticals on the TiO_2 assisted photocatalytic degradation rate of clofibric acid in aqueous suspensions.

2. Experimental

2.1. Chemicals and materials

Clofibric acid, carbamazepine, 10,11-dihydro-carbamazepine-10,11-epoxide and 10,11-dihydro-carbamazepine were purchased from Sigma–Aldrich (Deisenhofen), iomeprol was a courtesy from ALTANA (Konstanz). *p*-Benzoquinone, hydroquinone, phenol, 4-chlorophenol, isobutyric acid and phenylglyoxylic acid were purchased from Fluka (Deisenhofen) (all p.a. quality). All chemicals used for solutions (buffer, eluents, etc.) were reagent grade and were used without further purification. P25 was purchased from Degussa, and Hombikat UV100 was a courtesy gift from Sachtleben Chemie.

2.2. Analysis

The concentrations of clofibric acid, carbamazepine, iomeprol and their degradation products were measured by high performance liquid chromatography (HPLC) using a HP 1090 LC (Hewlett Packard) equipped with a diode-array (DAD) and fluorescence detector (FLD). The operating conditions for the HPLC/DAD/FLD measurements, the description of DOC (dissolved organic carbon) and AOX measurements are given elsewhere [14].

The separation of I^- and iomeprol was performed by ion chromatography with LC (Sykam, Germany) using an IonPac®AS9-SC (250 mm × 4 mm, Dionex) analytical column. Iodine was detected on-line with ICP-AES (Vista-Pro CCD Simultaneous ICP-OES, Varian) at 178.215 nm, with a detection limit of 50 μg/L. A 8 mM $NaHCO_3$ and 8 mM Na_2CO_3 solution in ultrapure water (18.2 MΩ cm, Milli-Q water, Millipore) was used as mobile phase. The flow rate was 1 mL/min, and the injection volume of the sample was 500 μL.

Isobutyrate and chloride were quantified by ion exchange chromatography on a DX 500 chromatographic system (Dionex), which was equipped with a GP40 gradient pump, an EG40 eluant generator and an AS40 auto sampler. Degassed (helium 5.0) ultrapure water was used for the production of the potassium hydroxide eluant in an eluant generator. The anion exchange column AS 11 (250 mm × 4 mm i.d.) and the guard column AG 11 (50 mm × 4 mm i.d.) were used for separating the analytes at room temperature. The detection system consisted of a conductivity detector (ED40, cell temperature 35 °C, temperature compensation 1.7 °C) and an anion self-regenerating suppressor (ASRS I) run in the auto suppression recycle mode at 300 mA. The operating conditions for the ion exchange chromatography were 0.2 mmol/L KOH during injection and for 5 min an isocratic analysis followed by a gradient analysis up to 31 mmol/L KOH in 6 min. After sample analysis it came a regeneration step and an equilibration step for 10 min with 35 mmol/L and for 10 min with 0.2 mmol/L, respectively.

Analysis for identification of further photocatalytic degradation products was performed with an Agilent 1100 HPLC system coupled by means of an electrospray ion source (TurboIon Spray, Applied Biosystems Sciex) to an Applied Biosystems Sciex API 3000 triple-quadrupole mass spectrometer. For analysis of the photocatalytic degradation products of clofibric acid like 2-(4-hydroxyphenoxy)-isobutyric, hydroxyisobutyric acid and 4-chlorohydroxyphenol a negative ion spray voltage and for degradation products of carbamazepine a positive ion spray voltage were used for ionization.

2.3. Sample preparation

Stock solutions were prepared by dissolving the pharmaceuticals and contrast media in ultrapure water. After addition of the pharmaceuticals, the samples were stirred for several hours to ensure complete dissolution. Then the stock solutions were filtered (0.2 μm cellulose nitrate filter). The stock solutions were protected from solar irradiation and stored in a refrigerator at 4 °C. Their ages were kept less than one month. For the irradiation experiments the TiO_2 suspension was freshly prepared by suspending TiO_2 in ultrapure water and then was sonicated for 30 min at least. Before starting the irradiation, the pharmaceutical or contrast media solution was equilibrated with humidified air in order to get defined concentrations of oxygen and bicarbonate in all samples, then mixed with the

sonicated TiO_2 suspension and adjusted to a defined pH value. After irradiation, the samples were filtered through a membrane (PVDF, Millipore) with a pore size of 0.1 μm. Two un-irradiated samples were taken always. One was filtrated after starting irradiation, the other one was stored as a system control at room temperature in the dark and treated at the same time as the irradiated samples. The mean value of both was the un-irradiated reference.

Extraction and enrichment were performed by solid phase extraction (SPE) with LiChrolut RP18 cartridges (500 mg adsorbent, Merck). The cartridges were preconditioned with 1-propanol (8 mL), and ultrapure water (6 mL). For extraction, the irradiated and un-irradiated carbamazepine samples (40 mL) were sucked through the preconditioned sorbent at a flow rate of approximately 5 mL/min. After sample extraction the adsorbent was washed with ultrapure water (3 × 3 mL) to remove salts and was dried with air. The adsorbed compounds were subsequently eluted with 1-propanol (6 mL). These samples were evaporated to dryness with a gentle stream of nitrogen and the residue was dissolved in an acetonirile:ultrapure water (1:4) mixture (2.5 mL). An enrichment factor of 16 was achieved. The percentage recovery for carbamazepine was 78.4% with a standard deviation 5.2% ($n = 5$).

2.4. Irradiation experiments

The samples were irradiated using a Solar UV Simulator (Oriel Corp., Stratfort, CT). The scheme and a detailed description of the solar simulator used for irradiation experiments is given elsewhere [14]. The radiation source was a 1000 W Xe short-arc lamp. The spectral irradiance of the simulated solar radiation was determined by spectral radiometry in combination with polychromatic actinometry. The spectrum of the Solar UV Simulator contained relatively small portions of the visible light compared to the real sunlight, while the cut-off wavelength in the UV-range was situated at the same wavelength as in real sunlight. The intensities in the UV-range of the Solar UV Simulator are higher than those of the real sunlight [14]. The incident photon flux was determined by chemical polychromatic actinometry, using phenylglyoxylic acid dissolved in ACN:ultrapure water = 3:1 (v/v), which functions as an actinometer by the photochemical decarboxylation of phenylglyoxylic acid to benzaldehyde and carbon dioxide [15]. In the kinetics experiments the incident photon flux in the UV radiation range $\lambda < 400$ nm was 1.35×10^{-4} Einstein/(m^2 s), which is 1.3 times higher than the solar irradiation in the UV radiation range $\lambda < 400$ nm in central Europe in June. Up to 9 samples, which were open to atmospheric air, were irradiated simultaneously from above in a homogeneous light field. The sample volumes were 20 mL with an additional stirrer bar volume of 0.85 mL. The optical pathlength of the samples was 1.7 cm with a surface area of 12.1 cm^2. The samples were kept at constant temperature (20 °C ± 2 °C) by circulating water and stirred magnetically.

2.5. Adsorption experiments

Adsorption experiments were done in bottles by shaking the samples overhead for 48 h protected from light. The adsorption experiments were done by variation of the sorbate concentration (iomeprol $\rho_0 = 0.4$ to 25 mg/L, clofibric acid $\rho_0 = 0.1$ to 100 mg/L and carbamazepine $\rho_0 = 0.1$ to 25 mg/L) at constant TiO_2 concentration (1 g/L). The pH value of the solutions was 6.5. After the equilibration time, the samples were filtered through a membrane (PVDF, Millipore) with a pore size of 0.1 μm.

3. Results and discussion

The photochemical degradation (irradiation without TiO_2) of the persistent organic pollutants was studied [14]. It turned out to be negligible compared to their photocatalytic degradation. For example the photocatalytic degradation rate constant (k) of iomeprol with Hombikat UV100 was about 500 times higher than the photochemical degradation rate constant of iomeprol (Fig. 1).

3.1. Clofibric acid

The photocatalytic degradation of clofibric acid with two different concentrations of P25 or Hombikat UV100 during irradiation is given in Fig. 2. As expected, the effect of the TiO_2 concentration on the degradation kinetics was significant, confirming the positive influence of the increased number of TiO_2 active sites on the process kinetics. The photocatalytic degradation of various organic compounds by means of illuminated TiO_2 can be formally described by the Langmuir–Hinshelwood (L–H) kinetics model (Eq. (1)) [13]. Where dc/dt is the rate of degradation, k_a the apparent reaction rate constant, K the adsorption coefficient of the substance to be degraded and c its concentration at time 0 and t.

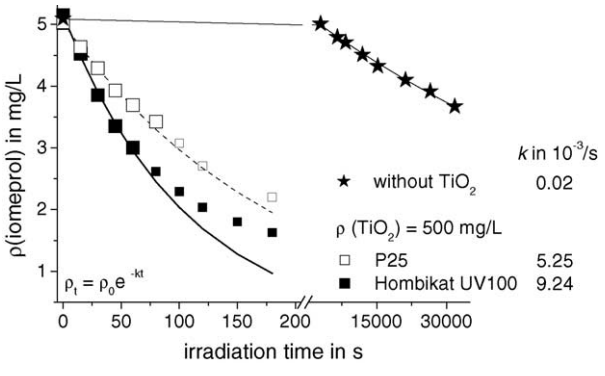

Fig. 1. Changes of concentrations of iomeprol ($\rho_0 = 5.2$ mg/L, pH 6.5) during irradiation without and with suspended TiO_2 (Hombikat UV100 or P25, $\rho(TiO_2) = 0.5$ g/L). For the determination of the first order rate constant (k) only the concentration values with $\rho_t/\rho_0 \geq 0.5$ (large symbols) were used. The fitting was done by the least squares method.

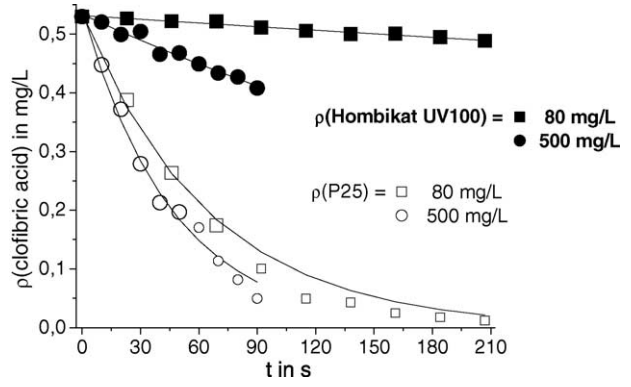

Fig. 2. Decrease of clofibric acid concentration ($\rho_0 = 0.53$ mg/L, pH 6.5) during irradiation. For the data fit by a first-order kinetic equation only the concentration values with $\rho_t/\rho_0 \geq 0.5$ (large symbols) were used, because the degradation products influenced the rate in the sequel by competitive photocatalytic degradation. The fitting was done by the least squares method.

$$-\frac{dc}{dt} = \frac{k_a K c}{1 + Kc} \quad (1)$$

The L–H equation simplifies for low concentrations of pollutants ($Kc \ll 1$) to a pseudo-first-order kinetic equation (Eq. (2)) where k is the pseudo-first-order rate constant.

$$-\frac{dc}{dt} = kc \quad \text{or} \quad c_t = c_0 e^{-kt} \quad (2)$$

In case of photocatalytic degradation of clofibric acid with Hombikat UV100 the decrease of clofibric acid concentration follows a zero-order kinetic equation. To compare the photocatalytic degradation rate constants of both TiO_2 materials, all data sets were fitted by a first-order kinetics equation. With P25 used as photocatalyst, the degradation of clofibric acid was faster than with Hombikat UV100 (Fig. 2). The photocatalytic degradation rate constant (k) for the pseudo-first-order degradation kinetics of clofibric acid ($\rho_0 = 0.53$ mg/L) for P25 and Hombikat UV100 ($\rho(TiO_2) = 0.08$ or 0.5 g/L) was 0.4×10^{-3} or 17.3×10^{-3} 1/s and 2.8×10^{-3} or 22×10^{-3} 1/s, respectively. According to the degradation experiments the adsorption capacity of P25 for clofibric acid was higher than for Hombikat UV100 (Table 1).

During the photocatalytic degradation with P25 ($\rho = 0.5$ g/L), the clofibric acid concentration and the AOX concentration decreased within 45 min from $c_0 = 0.93$ to 0.26 mmol/L and from 0.93 to 0.66 mmol/L, respectively (Fig. 3). After 40 min irradiation the DOC concentration decreased from $\rho(DOC)_0 = 111.9$ to 83.6 mg/L, but the

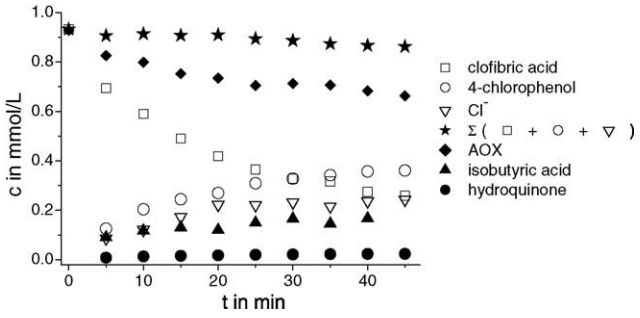

Fig. 3. Photocatalytic degradation (ρ(P25) = 0.5 g/L; pH 3.4) of the clofibric acid ($\rho_0 = 200$ mg/L) vs. irradiation time. Clofibric acid and its degradation products like 4-chlorophenol, hydroquinone, isobutyric acid, chloride and AOX are given as molar concentrations. The sum of chloride, clofibric acid and 4-chlorophenol is also given.

calculated sum of clofibric acid (ρ(DOC of clofibric acid) = 23.9 mg/L) and his quantified degradation products (ρ(DOC) for 4-chlorophenol = 25.7 mg/L, isobutyric acid = 8.0 mg/L and hydroquinone = 1.7 mg/L) reached only the theoretical DOC concentration of 68.3 mg/L. The data show that there was still an amount of not identified and quantified intermediates, which contribute to the measured DOC. The DOC and AOX concentration did not decrease as rapidly as the clofibric acid concentration, indicating a fast transformation of clofibric acid but not a fast dechlorination and/or mineralization. After the irradiation time of 45 min, the AOX concentration as a sum parameter of the chlorinated organic compounds and the sum of the quantified chlorinated products concentrations were 0.66 and 0.62 mmol/L (c(clofibric acid) = 0.26 mmol/L + c(4-chlorophenol) = 0.36 mmol/L), respectively (Fig. 3).

These data shows that there was still an amount of not identified and not quantified chlorinated intermediates, which contribute to the measured AOX. Also the balance of chlorine as the sum of chloride and quantified chlorinated compounds show that not all applied chlorine was quantified (Fig. 3). The increasing Cl^- concentration over the irradiation time indicates the dechlorination of clofibric acid and its chlorinated degradation products. The measured molar Cl^- increase was equivalent to the molar AOX decrease during irradiation (Fig. 3). This indicates that, during irradiation and analysis, no evaporation of chlorinated volatile compounds took place.

For comparison, during the photocatalytic degradation with Hombikat UV100 ($\rho = 0.5$ g/L), the clofibric acid concentration and the AOX concentration decreased within

Table 1
Freundlich constant K_F and exponent n for Hombikat UV100 and P25 for different persistent organic pollutants (R^2: correlation coefficient)

Polar persistent organic pollutant	K_F in (mg/g) (L/mg)^n	
	P25	Hombikat UV100
Iomeprol	0.196 ± 0.026, $n = 0.962$, $R^2 = 0.989$	0.767 ± 0.008, $n = 0.965$, $R^2 = 0.999$
Clofibric acid	0.06 ± 0.02, $n = 1.082$, $R^2 = 0.947$	0.04 ± 0.01, $n = 1.529$, $R^2 = 0.977$
Carbamazepine	0.042 ± 0.009, $n = 0.711$, $R^2 = 0.959$	0.041 ± 0.004, $n = 0{,}691$, $R^2 = 0{,}990$

45 min from c_0 = 0.795 to 0.640 mmol/L and from 0.795 to 0.79 mmol/L, respectively. The measured DOC concentration decreased within 40 min from $\rho(DOC)_0$ = 95.4 to 91.2 mg/L, but the calculated sum after 40 min irradiation of clofibric acid (ρ(DOC of clofibric acid) = 78.5 mg/L) and its quantified degradation products (ρ(DOC) for 4-chlorophenol = 10.43 mg/L and isobutyric acid = 1.8 mg/L) reached the theoretical DOC concentration of 90.7 mg/L. After the irradiation time of 45 min the AOX concentration as sum parameter of the chlorinated organic compounds and the sum of the chlorinated quantified products was 0.79 mmol/L and 0.79 mmol/L (c(clofibric acid) = 0.64 - mmol/L + c(4-chlorophenol) = 0.15 mmol/L), respectively. The data show that there was a small amount of not identified and quantified intermediates which contribute to the measured DOC and that the concentrations of other chlorinated degradation products must be very low.

The degradation products were assigned according to the retention times in the liquid chromatogram and the UV spectra based on comparison with standards. The degradation compounds, which were not identified or quantified by standards over the retention time and their corresponding UV spectra, were characterized by interpretation of their mass spectra. Further possible photocatalytic degradation products of clofibric acid like 2-(4-hydroxy-phenoxy)-isobutyric acid (m/z195), hydroxyisobutyric acid (2-hydroxyisobutyric acid or 3-hydroxyisobutyric acid (m/z 103) and 4-chlorohydroxyphenol (certainly 4-chloro-catechol) (m/z 143, 145 ratio 3:1) were tentatively identified. All facts indicate that photocatalysis is able to transform clofibric acid to degradation products which might have changed their former properties, like persistence to biodegradation. It is supplementary a powerful technique to mineralize clofibric acid. With P25 used as photocatalyst, the degradation of clofibric acid was faster than with Hombikat UV100, but the same intermediates were detected in both cases.

To check the more complex situation in real waste and raw water, the influence of carbamazepine and of NOM (HO19) from a bog water lake on the photocatalytic degradation of clofibric acid was investigated (Fig. 4). The photocatalytic degradation of clofibric acid in case of P25 is faster than in the case of Hombikat UV100, even in the presence of interfering substances. However, the retardation of the degradation of clofibric acid in the presence of NOM is stronger for P25 than for Hombikat UV100. Probably the adsorption of NOM from Lake Hohloh onto Hombikat UV100 was not so favored as onto P25. The adsorption of NOM from paper-mill effluents onto Hombikat UV100 was less than onto P25 [16]. The reaction rates for the photocatalytic degradation of NOM from paper-mill effluents were higher for P25 than for Hombikat UV100 [16]. Hombikat UV100 has also a greater specific surface area than P25 (>250 m^2/g and 50 ± 15 m^2/g, respectively), which makes the competitive adsorption more effective for the latter. In general the presence of NOM and other organic substances retarded the photocatalysis by the combination effects of radiation attenuation (competitive absorption), and competition for active sites or reactive species and the surface deactivation of the photocatalyst by adsorption.

3.2. Iomeprol

The photocatalytic degradation of iomeprol during irradiation is shown in Figs. 1 and 5. The kinetics of the iomeprol decay in the presence of the different types of TiO_2 (P25 and Hombikat UV100 ρ = 0.5 g/L) followed first-order degradation kinetics, which was consistent with the L–H model (Fig. 1). The photocatalytic degradation rate constant (k) for pseudo-first-order degradation kinetics of iomeprol for P25 and Hombikat UV100 were 5.25×10^{-3} and 9.24×10^{-3} 1/s, respectively. From the

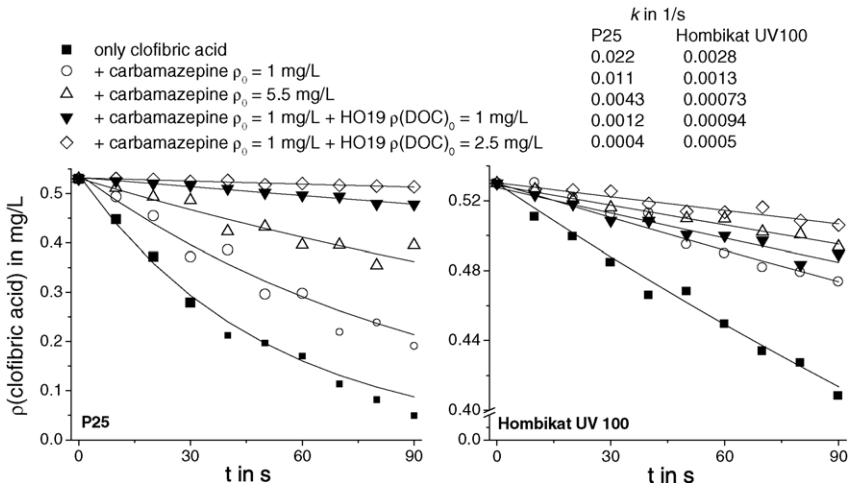

Fig. 4. Decrease of clofibric acid concentration (ρ_0 = 0.53 mg/L) during irradiation in presence of carbamazepine and of NOM (HO19) with suspended TiO_2 (P25 (left) and Hombikat UV100 (right), $\rho(TiO_2)$ = 0.5 g/L), pH 6.5. For the calculation of the first order degradation rate constants (k) only the concentration values with $\rho_t/\rho_0 \geq 0.5$ (large symbols) were used.

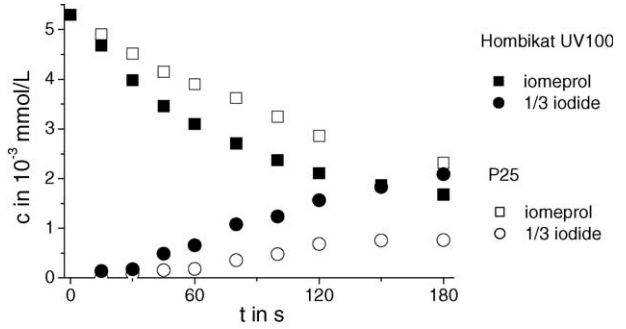

Fig. 5. Changes of concentrations of iomeprol ($c_0 = 0.0053$ mmol/L) and iodide during photocatalytic irradiation with suspended TiO_2 (Hombikat UV100 or P25, $\rho(TiO_2) = 0.5$ g/L).

experiment it could be derived that Hombikat UV100 was more effective for photocatalytic oxidation of iomeprol than P25. A reason for that could be the better sorbent function of Hombikat UV100 for iomeprol in comparison to P25 (Table 1). During the irradiation of the iomeprol/TiO_2 suspension the concentration of I^- increased (Fig. 5). After photocatalytic irradiation of 3 min, the elimination of the iomeprol concentration with P25 and Hombikat UV100 was 2.98×10^{-3} and 3.62×10^{-3} mmol/L, respectively. The formed I^- concentration for P25 was $3 \times 0.76 \times 10^{-3}$ mmol/L and for Hombikat UV100 it was $3 \times 2.09 \times 10^{-3}$ mmol/L. The eliminated iomeprol was theoretically de-iodinated with P25 and Hombikat UV100 for 25.5 and 57.7%, respectively. It can be derived that Hombikat UV100 is also more suitable for de-iodination of iomeprol than P25. The increasing I^- concentration over the irradiation time indicates the stepwise de-iodination of the tri-iodinated contrast media iomeprol and also the formation of partially iodinated intermediates during the photocatalytic degradation. The degradation products show up at lower retention times in the liquid chromatogram of the reaction mixture. These intermediates may be even better biodegradable.

3.3. Carbamazepine

The photocatalytic degradation rate constant (k) for the pseudo-first-order degradation kinetics of carbamazepine ($\rho_0 = 4.3$ mg/L) for P25 and Hombikat UV100 (0.1 g/L) was 4.7×10^{-3} and 0.13×10^{-3} 1/s, respectively. With P25 used as photocatalyst the degradation of carbamazepine was faster than with Hombikat UV100, but no new intermediates were detected in latter case. According to the degradation experiments the adsorption capacity of P25 for carbamazepine (Table 1) was not much higher than for Hombikat UV100. Photocatalysis is a powerful technique to transform or mineralize carbamazepine. The degradation products show up in the liquid chromatogram of the reaction mixture at lower and higher retention times as carbamazepine. The degradation products were assigned according to the retention times in the liquid chromatogram and the UV spectra based on comparison with the standards (10,11-dihydro-carbamazepine-10,11-epoxide and 10,11-dihydro-carbamazepine). By this 10,11-dihydro-carbamazepine-10,11-epoxide (m/z 253) was identified as a degradation product of carbamazepine. The degradation compounds which could not be identified by authentic substances according to their retention time and their corresponding UV spectra were characterized by interpretation of their mass spectra. Further possible photocatalytic degradation products of carbamazepine like hydroxycarbamazepine (m/z 253), dihydroxycarbamazepine (m/z 269), acridine (m/z 180), acridine-9-carboxaldehyd (m/z 208), hydroxyacridine-9-carboxaldehyd ($m/z = 224$) and hydroxyacridine-9-carboxalcohol (m/z 226) were tentatively assigned. All facts indicate that photocatalysis is able to transform carbamazepine to degradation products showing other ecological properties, concerning persistence and biodegradation. e.g. acridine belongs to the azaarenes, an established class of air and water pollutants with mutagenic and cancerogenic activity [17].

Based on the structure identification of organic degradation products, a possible photocatalytic degradation pathway for carbamazepine is proposed in Fig. 6. The great number of compounds detected during the photocatalytic degradation of carbamazepine shows the complexity of the reactions involved in photocatalysis, and suggests the existence of various degradation routes resulting in multi step and interconnected pathways. This work points to the necessity of extended knowledge of the successive steps in light-assisted photocatalytic degradation/detoxification processes.

3.4. Adsorption

Isotherms were determined to investigate how the degradation rates of the two different TiO_2 materials are influenced by the different adsorbent behavior of the photocatalysts. The data evaluation according to Freundlich's isotherm showed a good curve fitting for all data. The Freundlich constant K_F of the Hombikat UV100 and P25 for all persistent organic pollutants are given in Table 1. For example the Freundlich constant K_F of the Hombikat UV100 was 4 times higher than the one of P25, which clearly reveals the higher adsorption capacity of Hombikat UV100 for iomeprol. This goes parallel with a better photocatalytic degradation of iomeprol by Hombikat UV100 (Figs. 1 and 5). The Freundlich constant K_F of P25 was a bit higher than the one of the Hombikat UV100, which also reveals the better adsorption capacity of P25 for clofibric acid. This correlates with a better photocatalytic degradation of clofibric acid alone (Fig. 2) and also in presence of competing substances (Fig. 4) by P25. The photocatalytic degradation for carbamazepine was better on P25 than on Hombikat UV100. However, there was no significant difference in the adsorption behavior. Probably there was a better photoadsorption of carbamazepine on P25 than on

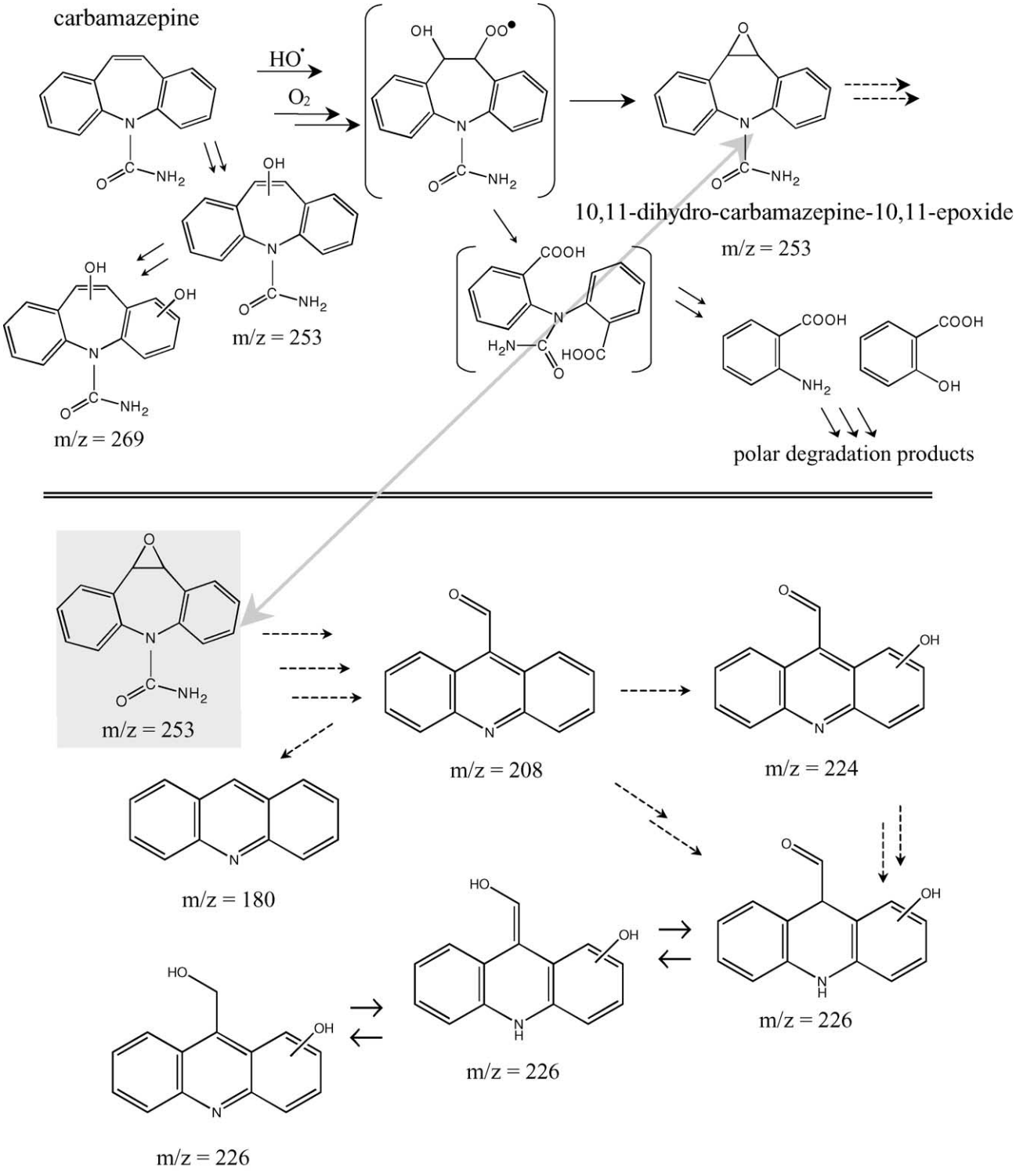

Fig. 6. Suggested simplified degradation scheme for the photocatalytic degradation of carbamazepine.

Hombikat UV100. The adsorption experiments were done in the dark that means the adsorption capacity cannot be transferred quantitatively into irradiated systems. Nevertheless, a qualitative estimation from the adsorption experiments to the photocatalytic activity of a photocatalyst is possible.

4. Conclusions

Semiconductor photocatalysis appears to be a promising technology to degrade carbamazepine, clofibric acid, iomeprol and NOM even if they are simultaneously present. Transformation, deactivation and minimization of envir-

onmentally persistent compounds can be achieved. Photocatalysis as a treatment step should enhance the biodegradability of the pollutants, but does not requires a complete mineralization. As a consequence the combination of photocatalysis and a subsequent biological treatment step can be favorably applied for advanced water treatment. On the other hand the identification of possibly formed highly toxic compounds is essential for a sound assessment of the treated water. The application of the photocatalysis in the real world of wastewater and raw water treatment should be further investigated by means of a pilot plant. Also the long-term behavior of the photocatalysts needs to be studied.

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