



Impact of water quality on removal of carbamazepine in natural waters by N-doped TiO₂ photo-catalytic thin film surfaces

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H I G H L I G H T S

- ▶ N-doped TiO₂ thin films have been deposited by sol-gel dip-coating.
- ▶ CBZ removal improved with increasing medium pH in the range of 5–9.
- ▶ DOC at a concentration of 5 mg/L resulted in an ~20% reduction in CBZ removal.
- ▶ Alkalinity values of 100 mg/L as CaCO₃ resulted in a 40% decrease in CBZ removal.
- ▶ Complete suppression of the photocatalytic process in wastewater effluent.

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Photocatalytic experiments on the pharmaceutical pollutant carbamazepine (CBZ) were conducted using sol-gel nitrogen-doped TiO₂-coated glass slides under a solar simulator. CBZ was stable to photodegradation under direct solar irradiation. No CBZ sorption to the catalyst surface was observed, as further confirmed by surface characterization using X-ray photoelectron spectroscopic analysis of N-doped TiO₂ surfaces. When exposing the catalyst surface to natural organic matter (NOM), an excess amount of carbon was detected relative to controls, which is consistent with NOM remaining on the catalyst surface. The catalyst surface charge was negative at pH values from 4 to 10 and decreased with increasing pH, correlated with enhanced CBZ removal with increasing medium pH in the range of 5–9. A dissolved organic carbon concentration of 5 mg/L resulted in ~20% reduction in CBZ removal, probably due to competitive inhibition of the photocatalytic degradation of CBZ. At alkalinity values corresponding to CaCO₃ addition at 100 mg/L, an over 40% decrease in CBZ removal was observed. A 35% reduction in CBZ occurred in the presence of surface water compared to complete suppression of the photocatalytic process in wastewater effluent.

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1. Introduction

The legal discharge of low concentrations of pharmaceutical residues from point and non-point sources to receiving waters [1] has resulted in some of these contaminants ending up in irrigation water, potentially leading to groundwater contamination [2,3]. In the European Union (EU) today, ~3000 different substances are used in medicines such as painkillers, antibiotics, contraceptives, beta-blockers, lipid regulators, tranquilizers, and impotence drugs. Frequently used pharmaceuticals (the

anti-epileptic carbamazepine—CBZ) and analgesic anti-inflammatory drugs (ibuprofen, diclofenac, ketoprofen and naproxen) have been detected in lakes, rivers and wastewater-treatment plant effluents in Switzerland, at concentrations ranging between 5 and 3500 ng/L [4]. To meet the increasingly rigorous water-quality standards, advanced treatment technologies for water and wastewater treatment plants need to be developed and adopted.

In advanced oxidation processes (AOPs), pollutants are chemically oxidized by nonselective hydroxyl free radicals. The versatility of the AOPs is enhanced by the different ways in which hydroxyl radicals can be produced, facilitating compliance with the specific treatment requirements. Homogeneous UV- and ozone-based AOPs can produce hydroxyl radicals in the combinations H₂O₂/UV, O₃/UV, H₂O₂/O₃/UV, O₃/H₂O₂. Other methods, such as

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heterogeneous photocatalysis and homogeneous photo-Fenton, are based on the use of a wide-band gap semiconductor and addition of H_2O_2 to the dissolved iron salts, respectively, and irradiation with UV–vis light.

The use of semiconductors in combination with sunlight irradiation (i.e. photocatalysis) for the treatment of water and wastewater has attracted growing attention and intense research interest in the last decade [5]. Semiconductors can be excited by light with higher energy than the band gap to generate energy-rich electron–hole pairs. The photogenerated holes and electrons can recombine or make their way to the catalyst surface, where they can react with and degrade adsorbed target pollutants or form reactive oxygen species (e.g. OH^\bullet radicals). TiO_2 is the most widely used photocatalyst, mainly due to its high efficiency, photochemical stability, nontoxic nature and low cost [6].

TiO_2 has been widely applied to remove trace micropollutants (e.g. pharmaceuticals) from water [7–9] and wastewater effluent [10,11], and as a water disinfectant [12,13]. The main limitation of TiO_2 is a relatively wide band gap (3.02 eV for rutile, 3.2 eV for anatase) [14], which results in about 5% spectral overlap between its absorbance and sunlight emission ($\lambda < \sim 390$ nm). Different attempts to overcome this drawback have made use of physical and chemical means such as morphological modifications to increase active surface area [15], use of other semiconductors such as WO_3 or ZnO , used with TiO_2 or as independent catalysts [16,17], and doping the TiO_2 with different elements, such as nitrogen. Asahi et al. [18] were one of the first to describe N-doped TiO_2 materials. N doping showed effective UV and visible light activity.

CBZ is used for the treatment of seizure disorders, for the relief of neuralgia, and for a wide variety of mental disorders [19]. This drug is the most frequently detected pharmaceutical in various water sources. Usually, CBZ is excreted with <3% remaining in its unaltered form and flushed directly to the wastewater treatment plants (WWTPs) through the sewage system [20]. Studies have determined that CBZ is persistent, with removal efficiencies by the WWTPs are being mostly below 10% [21]. In the classification scheme for pharmaceutical biodegradation, CBZ has the status of “no-removal” [22]. Clara et al. [23] and Kosjek et al. [20] reported that CBZ is resistant to biodegradation and shows almost no elimination during conventional wastewater treatment. Specifically, Kosjek et al. [20] reported poor biological removal efficiency of CBZ by activated sludge together with the enhanced biodegradability of carbamazepine residues by medium-pressure UV irradiation, while ClO_2 treatment proved to be less efficient in comparison to UV for CBZ. Additionally, Okuda et al. [24] compared biological treatment processes as activated sludge and biological nutrient removal. Generally the total concentration of the individual pharmaceuticals in the influent was efficiently removed by 80% during the biological treatment. But removal efficiency of carbamazepine was less than 30%. Moreover, coagulation, sedimentation and filtration followed by UV or chlorination disinfection after the above biological processes, was not efficient for pharmaceuticals removal.

Furthermore, alternative technics such as ozonation [25–27] and technics based on AOPs as UV/ H_2O_2 [28–30], UV/ TiO_2 [7,31] and fenton [32,33] showed promising results toward removing CBZ among other organic pollutants.

Photocatalytic efficiency is expected to be lower for natural water. This is due to the water's chemical composition, particularly the photoactive and inhibitor compounds present in different water bodies, which have a substantial impact on reaction pathways. Moreover, natural organic matter (NOM) and alkalinity are expected to be the main inhibitors of photocatalytic degradation of micropollutants as they may absorb photons and scavenge radicals, reducing the formation of more reactive oxidation species (e.g. OH^\bullet) [34,35].

This paper addresses the effects of the interaction between water characteristics and the photocatalytic surface on the photodegradation of target organic pollutants. The main objectives of this study were to (a) examine the influence of NOM and water contaminants on the photocatalytic efficiency of a sol–gel N-doped TiO_2 surface on CBZ, (b) characterize the streaming potential and hydrophobicity of the coated surface and their correlation to CBZ removal, and (c) determine the photocatalytic degradation of CBZ under various conditions (pH, NOM, alkalinity) and water types (surface, ground and wastewater effluents).

2. Materials and methods

2.1. Materials and reagents

Carbamazepine (>99% purity) was obtained from Sigma–Aldrich; LC–MS grade methanol and water were from Bio-Lab Ltd. (Jerusalem, Israel). HPLC-grade formic acid (Bio-Lab) was used to adjust pH during HPLC/MS analyses. All chemicals were used as obtained and CBZ stock solution was prepared by dissolving the compound in deionized (DI) water (Direct-Q3 UV System, Millipore, France) at a concentration of 50 mg/L. Suwannee River NOM was obtained from the International Humic Substances Society (IHSS). CaCO_3 was prepared from a stock solution of dissolved NaHCO_3 .

2.2. Preparation and characterization of N-doped TiO_2 coatings

Precursor solutions for N-doped TiO_2 coatings were prepared with tetrabutylorthotitanate, isopropanol, ammonium hydroxide and triethanolamine [36]. Tetrabutylorthotitanate (25 mL) and triethanolamine (15 mL) were dissolved in isopropanol (32 mL), together with ammonium hydroxide (32%, 2.4 mL). After stirring vigorously for 30 min at room temperature, the solution was ready for use. The substrates (standard microscope glass slide 75 mm \times 25 mm \times 1.5 mm) were carefully cleaned by ultrasonic treatment with acetone and air-dried. The N-doped TiO_2 coatings were prepared by a dip-coating method, with a withdrawal speed of about 1 mm/s. To dry the samples, the coated substrates were left for 5 min at 100 °C in the dip system before removing them. Then they were dried at 150 °C for 12 h in air; the temperature was raised at 3 °C/min to 510 °C and the samples were kept at this temperature for 1 h to allow the film to crystallize in anatase phase, as confirmed by X-ray diffraction measurements (data not shown).

X-ray photoelectron spectroscopy (XPS) surface analysis of sol–gel N-doped TiO_2 coatings was carried out using a Thetaprobe instrument (Thermo Fisher, East Grinstead, UK). Each sample was analyzed using Al $K\alpha$ X-rays ($h\nu = 1486.6$ eV) at a power of 140 W with a spot size of 400 μm , the analyzer being operated in constant energy mode at a pass energy of 300 eV for the survey spectra and 20–50 eV for the high-resolution spectra (C1s, O1s, N1s, Ti2p, Ca2p, P2p and Si2p). When necessary, and to record traces levels, the pass energy was increased to 200 eV. The pressure in the analytical chamber was on the order of 10^{-7} mbar during the analysis as charge compensation using argon bleeding within the chamber was used. Quantitative surface analyses were calculated from peak areas, using the appropriate instrument modified sensitivity factors and the manufacturer's AVANTAGE software v4.84.

Hydrophilicity of the N-doped TiO_2 film was measured using the captive air bubble method by immersing the surface in DI water and air bubbles were introduced to the chamber by pressure. The surface zeta potential was measured using a streaming potential analyzer (SurPass Elektrokinetic Analyzer, CT, USA) after equilibration with the NaCl solutions. The zeta potential of the

catalytic coated glass samples was calculated from the streaming potentials using the Helmholtz–Smoluchowski equation with the Fairbrother and Mastin substitution [37]. Streaming potential of the N-doped TiO₂ film was measured as a function of pH in a 1 mM NaCl solution.

2.3. Experimental setup

N-doped TiO₂ coatings were immersed in a 90 mm × 50 mm Pyrex glass plate containing 30 mL aqueous solution (DI water) of CBZ (diluted from stock solution to an initial concentration of 1 mg/L, 4.24×10^{-6} M). Unless otherwise indicated, experiments were carried out at neutral pH (7) adjusted using 1 mM phosphate buffer saline (PBS) (Na₂HPO₄/NaH₂PO₄). The examined solution was stirred for 60 min in the dark to ensure adsorption/desorption equilibrium of CBZ on the catalyst prior to its irradiation under a solar simulator for 90 min. Samples of 0.25 mL were taken periodically and analyzed by HPLC to quantify the CBZ concentration. All experiments were performed in triplicate and relative standard deviations were less than 10%. Specifically to determine the influence of pH, PBS (10 mM) was used in different ratios of Na₂HPO₄ to NaH₂PO₄. The photocatalytic efficiency was expressed as percent removal:

$$\text{Removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the initial pollutant concentration and C_t is the pollutant concentration after t hours of irradiation (mg/L). Additional UV photolysis experiments were carried out in a bench-scale collimated beam apparatus using a 0.45-kW polychromatic medium-pressure (MP) Hg vapor lamp (Ace-Hanovia lamp, Ace Glass Inc., Vineland, NJ, USA). Absorption for each water sample as a function of wavelength was measured by a CARY 100Bio Spectrophotometer.

2.4. Photocatalytic degradation experiments

Solar irradiation experiments were carried out in a 150-W xenon arc lamp solar simulator (Sciencetech Inc., ON, Canada). The light beam was filtered with an air mass (AM) 1.5 Global filter that simulates the total (direct and diffuse) solar spectrum equivalent to natural sunlight at 48.2° latitude at sea level. Irradiance was measured using a calibrated spectroradiometer (International Light, Model ILT 900R, MA, USA), placed in the same position as the irradiated solution. Fig. 1 shows the similarity between the spectra obtained from the solar simulator and natural sunlight.

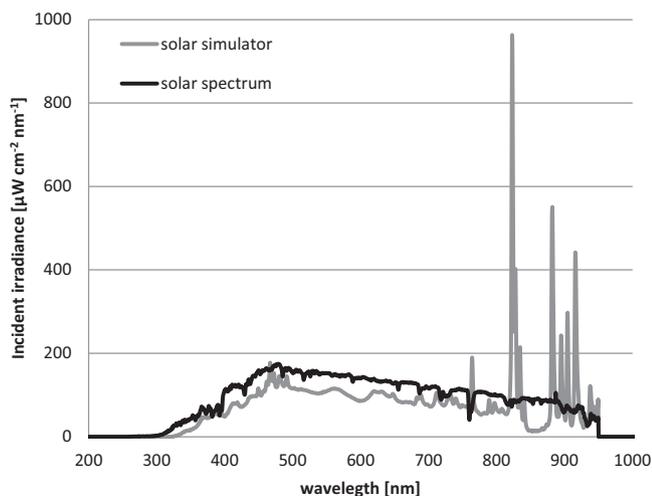


Fig. 1. Comparison of spectra obtained from the solar simulator and natural sunlight.

Total incident irradiance integrated between 280 and 950 nm was 500 W/m², including UVA irradiance of 21.5 W/m² and UVB irradiance of 0.9 W/m².

2.5. Chemical analysis

CBZ was detected and quantified by HPLC Agilent 1100 (ACE-RP Phenyl column 2.1 mm × 250 mm) with a diode array detector. The flow rate was set to 0.5 mL/min and the injected volume was 50 μL. The mobile phase consisted of water (A) and methanol (B), at pH 3. The mobile phase eluent gradient started with 60% of eluent A, followed by a 2-min linear gradient to 10% eluent A, 4-min isocratic elution and a 2-min linear gradient back to 60% eluent A, maintained for 5 min to equilibration.

2.6. Water type and analysis

Groundwater samples were taken from a local site of the major carbonate aquifer in the eastern slopes of the Judea Mountain Ridge in central Israel. Natural surface water was sampled from Lake Kinneret (Sea of Galilee) located in northern Israel, and from part of the Israeli water network supply. Secondary and tertiary wastewater was sampled from the Dan Region Wastewater Treatment Plant (Shafdan), which is a complex inter-regional system that treats and reclaims municipal wastewater in high-density urban areas and industrial zones. The tertiary effluent was obtained after in-line granular filtration with ferric chloride.

Alkalinity was determined by titration method using HACH digital titrator model 16900 (method 8203) [38], total hardness was determined by titration (method 8213) [38], and chloride was determined by titration (method 8206) [38]. Turbidity was measured using a HACH 2100Q portable turbidometer. The dissolved organic carbon (DOC) fraction was determined as the carbon concentration in the water passed through a 0.45-μm pore size filter, and analyzed by a TOC analyzer (Apollo 9000 carbon analyzer; Teledyne-Tekmar, Cincinnati, OH, USA). The obtained DOC level was ~50% of the Suwannee River NOM.

3. Results and discussion

3.1. Sol-gel N-doped TiO₂ deposition and characteristics

“Sol-gel” describes a broad class of processes in which a solid phase is formed through gelation of a colloidal suspension. N-doped TiO₂ sol-gel coatings were prepared by hydrolysis of Ti-alkoxide in alcohol solutions containing N compounds. N-doped TiO₂ coatings were deposited on commercial microscope glass slides as substrates, and the coating efficiency was determined according to CBZ removal. The samples were studied by XPS, and the N1s spectra acquired with higher resolution and count rate are reported (Fig. 2). Despite the long acquisition time, the low signal-to-noise ratio indicated a very small N concentration, with a value of about 0.5% obtained by calculating the area under the XPS peaks (annealing in air). Another interesting result was the measured binding energy of the peak observed in the recorded spectra, which was about 400 eV, which has been attributed to interstitial doping [39].

Fabricated photocatalytic materials may have an advantage over powdered photocatalytic materials suspended in water. Conventional use of the latter requires homogeneous mixing of the powder in a batch or completely mixed system, separation after use, and an understanding of the impact of particle light scattering on photon distribution in the reactor.

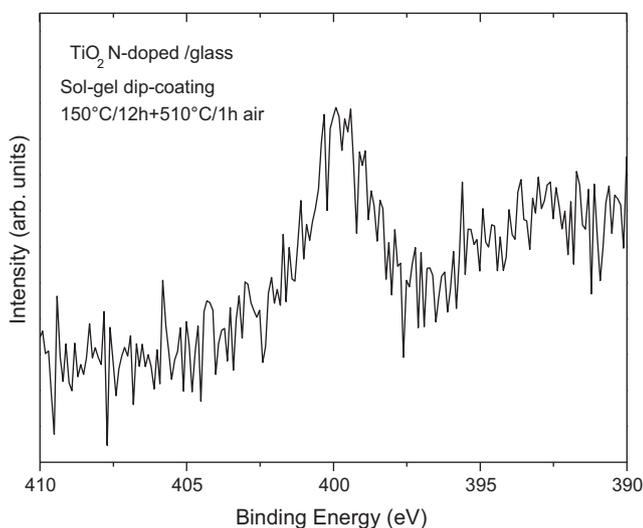


Fig. 2. XPS survey spectra of sol-gel N-doped TiO₂ samples after annealing in air.

3.2. Contact angle—wettability

The hydrophilicity of the sol-gel N-doped TiO₂-coated surfaces was measured via captive air bubble method, in which the surface is immersed in DI water and air bubbles are introduced into the chamber by pressure. The value of the air bubble contact angle of the coated surface in water was $36.9 \pm 7.6^\circ$, and $\sim 43^\circ$ on non-coated glass. Birdi et al. [40] reported a similar water contact angle of 41° on a glass surface. The contact angle for the N-doped catalytic surface suggests that it is relatively highly hydrophilic and can also explain the low adsorption of the organic molecule to the catalyst.

3.3. Streaming potential

The ionization state of the photocatalyst surface can also be protonated and deprotonated under acidic and alkaline conditions, respectively. At the point of zero charge (Pzc), the total negative and positive charge of the catalyst is zero. The Pzc of TiO₂ (Degussa P25) has been widely investigated and reported at pH 6.25 [41]. Under acidic conditions, the positive charge of the TiO₂ surface increases as the pH decreases; the negative charge of the TiO₂ surface increases with increasing pH. The pH of the solution affects the formation of hydroxyl radicals via the reaction between hydroxide ions and photoinduced holes on the TiO₂ surface.

Fig. 3 illustrates the streaming potential of the sol-gel N-doped TiO₂ films as a function of pH in a 1 mM NaCl solution. The streaming potential was negative at all pH values from 4 to 10 and decreased with increasing pH, indicating that the films are negatively charged at pH > 4 with an increase in negative charge at higher pH values, reaching a plateau at about pH 9.

3.4. Direct photolysis of CBZ under UV radiation and solar simulator

Most of the solar UV radiation reaching the earth's surface is UVA ($\sim 99\%$), since the ozone layer of the atmosphere absorbs the UVC and most of the UVB. Emission spectra of the 150-W Xenon solar simulator and 0.45-kW MP UV lamp, and the molar (decadic) absorption coefficient of CBZ in water at an initial CBZ concentration of 1 mg/L and pH 7, are shown in Fig. 4. CBZ absorbs light within the UVC and UVB range.

CBZ has been detected in wastewater [42–44], surface water [45–47], and groundwater [48,49]. The compound has shown little degradation or retention during bank filtration [50,51] or in

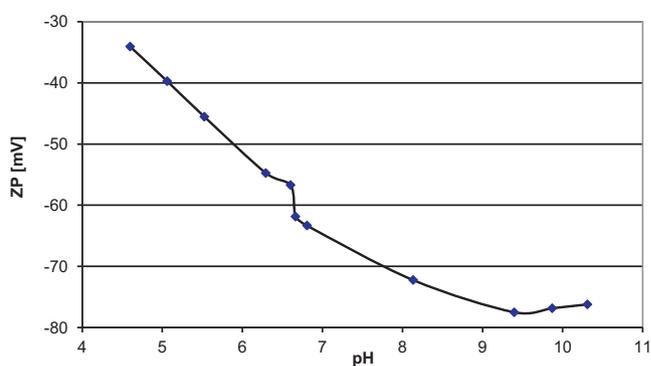


Fig. 3. Streaming potential (ZP) of sol-gel N-doped TiO₂ surface vs. pH in a 1 mM NaCl solution.

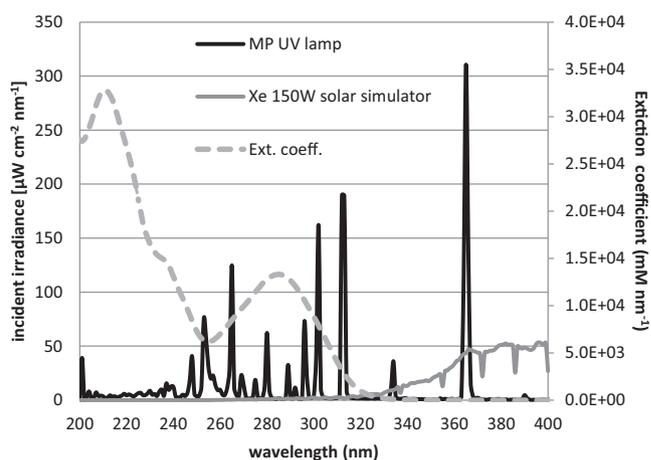


Fig. 4. Emission spectra of the 0.45-kW MP UV lamp, 150-W Xe solar simulator and extinction coefficient of CBZ in DI water at an initial CBZ concentration of 1 mg/L and pH 7.

sediment-transport studies [49]. CBZ has been used as a marker for groundwater contamination through sewer exfiltration by several research groups [48,52], and was therefore selected for this study.

Direct photodegradation of CBZ after 1 h exposure under the solar simulator was negligible (2%). However, under the MP UV lamp, CBZ underwent almost complete degradation after 60 min of irradiation (95%) (data not shown). This result was expected as CBZ's maximum absorbance is at 286 nm, which overlaps with the MP UV lamp output (Fig. 4). Doll and Frimmel [29] investigated the photodegradation of CBZ and other pollutants by simulated solar UV light and found 50% degradation of CBZ after ~ 15 h with a 1000-W Xe short-arc lamp (intensities of this solar UV simulator in the UV range are 1.9 times higher than those of natural sunlight). Matamoros et al. [53] found a half life of 38.5 h for CBZ in DI water. Indirect photolysis of CBZ under UV/H₂O₂ showed that CBZ is susceptible to degradation via hydroxyl radical-induced reactions (data not shown), making it a good candidate for photocatalytic degradation.

3.5. Adsorption of CBZ

Use of thin film coatings (as opposed to powders) should result in lower adsorption of molecules in the water to the catalytic surface due to lower surface area. Consequently, sorption of the catalyst to target pollutant molecules should be examined. CBZ, however, is a relatively polar, neutrally charged pharmaceutical that lacks sites for specific interactions with soils and sediments, leading to its non-appreciable sorption properties [23,49,54]. CBZ is

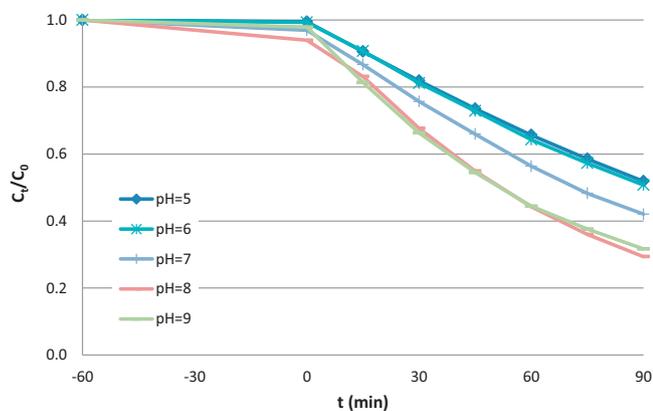


Fig. 5. Percent CBZ removal as a function of time at different medium pH.

not expected to adsorb to the catalyst surface by charge-attraction forces. Indeed, the surface was exposed to a solution of CBZ and, after 24 h of equilibrium, no sorption of CBZ was found. Moreover, no CBZ was found on the surface by XPS and ToF-SIMS (Section 3.7.1).

3.6. Influence of pH on photocatalysis

The photocatalytic activity of sol-gel N-doped TiO₂ coatings was tested at different pH values (5, 7, 8, 9) adjusted by 10 mM phosphate buffer saline (PBS) in water spiked with 1 mg/L CBZ. CBZ is a neutral molecule at a broad range of pH values, and therefore photocatalysis is affected by pH via the surface charge of the photocatalyst. Vogna et al. [28] investigated the AOP of CBZ with UV/H₂O₂ and found that CBZ degradation by radical-induced reaction is not affected by changing the pH of the solution in the range of 2.0–8.0. As already noted, the ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively.

The positive holes are considered the major oxidation species at low pH, whereas hydroxyl radicals are considered the predominant species at neutral or high pH [55,56]. The generation of OH• is expected to be higher due to the presence of more available hydroxyl ions on the catalyst surface. Thus, the degradation efficiency of the process is expected to be enhanced at high pH and Fig. 5, illustrating the removal of CBZ at different pH values, verifies this assumption. Obviously, photocatalysis increases with increasing pH up to pH 8 and at pH ≥ 8, the trend is moderated. This result is in good agreement with the data obtained from the streaming potential measurements of the photocatalyst surface and seems to be promising since surface water tends to be basic.

3.7. Catalyst efficiency in various water types

The chemical composition of natural waters has a substantial impact on reaction pathways due to the presence of scavenging, inhibiting and promoting compounds and their interaction with reactive species generated in the photocatalytic process. For example, Selvam et al. [57] reported a beneficial effect of transition metal ions on the degradation of 4-fluorophenol following the order: Mg²⁺ > Fe³⁺ > Fe²⁺ > Cu²⁺, and an inhibitory effect of inorganic anions on the degradation of 4-fluorophenol following the order: CO₃²⁻ > HCO₃⁻ > Cl⁻ > NO₃⁻ > SO₄²⁻. Initial experiments were conducted to simulate two prominent interfering substances in the water that might have an effect on photocatalysis: NOM and calcium carbonate.

NOM is a complex mixture of different organic chemicals originating from natural biological activity in water. NOM can

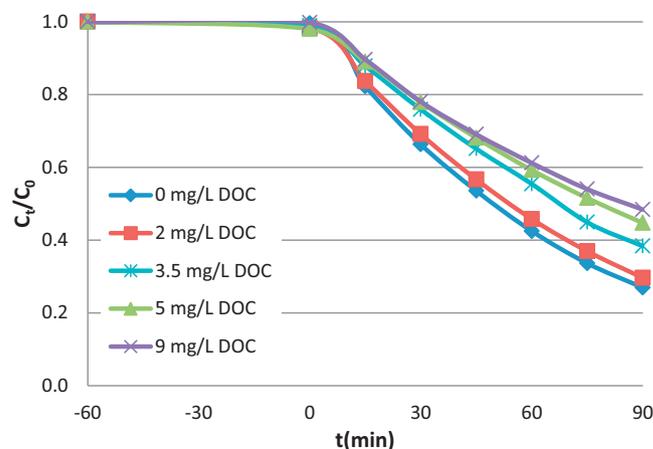


Fig. 6. Percent CBZ removal as a function of time at different DOC concentrations of NOM.

impact AOP efficiency via several mechanisms: light absorption, its activity as a radical inhibitor or promoter, depending on its functional groups and molecular size (as an inhibitor, NOM reacts with OH• radicals to form a nonreactive species, thus terminating the chain reaction, and as a promoter, NOM reacts with OH• radicals to form reactive species and secondary carbon-centered radicals [34], thus promoting the chain process), its potential adsorption to the catalyst surface, and its important role in sunlight-induced photochemical processes in surface waters.

Matamoros et al. [53] studied the photodegradation of CBZ and other compounds in fresh water and seawater and found that it increased in river waters; they linked this phenomenon to the high DOC content in the river water, which promotes indirect photodegradation by generation of photoreactants (e.g. ¹O₂, •O₂, H₂O₂, e_{aq}⁻, etc.). NOM can enhance CBZ degradation via indirect slow photodegradation in photocatalytic processes. Nevertheless, NOM can serve as an inner filter for incoming photons and can act as a radical scavenger, reducing the formation of reactive oxidation species (e.g. OH•) and consequently reducing process efficiency.

Fig. 6 shows the influence of different DOC concentrations (0, 2, 3.5, 5 and 9 mg/L) on CBZ photocatalysis (1 mg/L at pH 7). The low concentration of DOC (2 mg/L) had only a negligible effect on CBZ removal; at 5 mg/L DOC there was an approximate 20% reduction in CBZ removal (see Table 1). Doll and Frimmel [58] investigated the influence of NOM on photocatalytic degradation of organic compounds (e.g. CBZ) by TiO₂ (P25) and showed a 40% decrease in removal rate for only ~1 mg/L NOM. This difference can be explained by the high adsorption of NOM onto TiO₂ (P25). Mixing NOM with TiO₂ in the dark resulted in adsorption of 61% of the DOC onto the catalyst. Adsorption was negligible for the sol-gel N-doped coated samples.

A 5% reduction was observed in the average dose calculated by integrating the water absorbance for a 9 mg/L DOC solution (data not shown). Therefore, the decrease in CBZ photocatalytic degradation rate cannot be simply a consequence of the inner filter effect of NOM; another competitive reaction inhibiting photocatalytic degradation of CBZ must be occurring, since NOM consists of electron-rich compounds capable of scavenging the holes photo-generated in the catalyst valence band.

Table 1
Percent CBZ removal with different DOC concentrations after 90 min of exposure.

	DOC conc. (mg/L)				
	0	2	3.5	5	9
% Removal	70	68.3	59.6	53.2	49.5

Table 2
Comparison of surface composition in all batches (at.%).

Sample	C	O	N	Ti	Ca	Si
Control 1	14.2	48.5	0.4	16.6	–	–
Control 2	15.9	59.3	0.6	13.3	0.6	5.8
NOM	19.4	59.4	0.6	13.7	0.4	5.5

3.7.1. XPS surface analysis of sol-gel N-doped TiO₂ coating exposed to NOM

The surface composition, determined by XPS, is given in Table 2 in percentages. The samples were as follows: control is a sample immersed in HPLC-grade water, and NOM is a sol-gel sample immersed in 30 mL HPLC-grade water with NOM at a concentration of 18 mg/L. The XPS data, in general, indicated a very low amount of C—even less than the amount anticipated for simple adventitious surface contamination (expected level of atmospheric contamination usually due to minimization of surface energy). Therefore, the surfaces could be considered extremely clean and devoid of contaminants, in XPS terms.

The NOM sample exhibited a higher amount of C than the control samples. This is characteristic of the presence of adsorbed organic species. A careful analysis of the C signal of the control and NOM samples is shown in Fig. 7.

The C signal can be decomposed into four components at different binding energies: 285 eV (C–C, C–H), 286.4 eV (C–O, *C–O–C=O), 287.7–287.8 eV (O–C–O) and 289.1–289.4 eV (O=C–O). Of interest is the second component, which showed a significant increase after treatment with NOM and irradiation. The excess amount of the second C compared to the control is consistent with the remaining NOM material. Indeed, the water used originates from the Suwannee River, which is a blackwater river and hence contains tannins. This type of molecule has functionalities consistent with the presence of C–O and C–OH chemistry. The time needed to eliminate the pollutant might be higher or the coverage may influence the efficiency of the photocatalytic degradation of CBZ. In addition, surface characterization using XPS and Time-of-Light Secondary Ion Mass Spectrometry (ToF-SIMS) analysis of doped surfaces showed that the catalyst surface is clean and devoid of CBZ before and after photocatalysis (data not shown).

3.8. Alkalinity

To examine the effect of different concentrations of alkalinity on photocatalysis, different concentrations of bicarbonate (25, 50, 100, 200 and 300 mg/L as CaCO₃) were added to DI water spiked with 1 mg/L CBZ, while the pH value was naturally maintained between 9 and 9.5 by the bicarbonate in the solution.

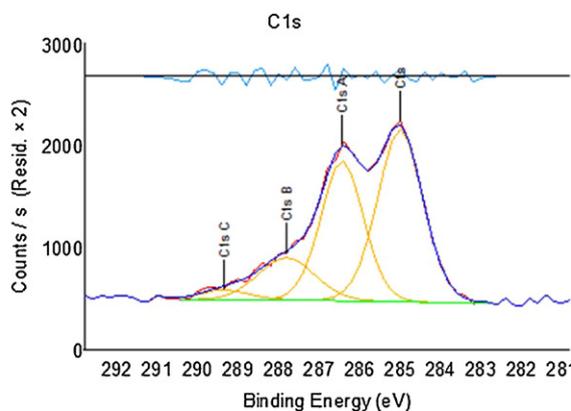
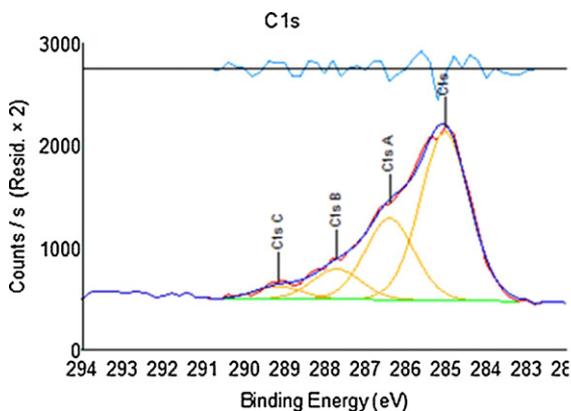


Fig. 7. Comparison of XPS C1s signal for control (left) and NOM sample (right).

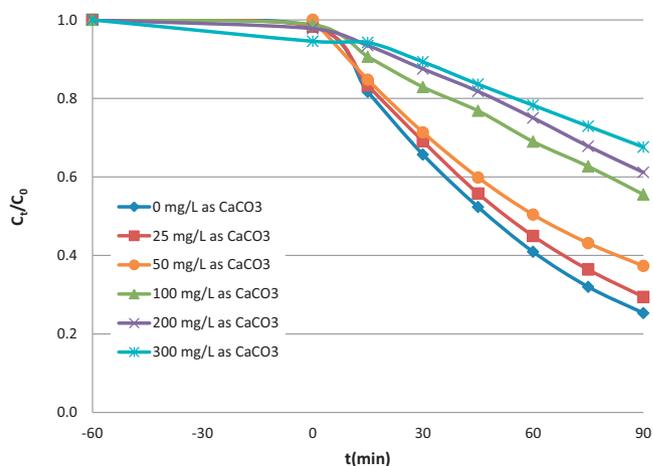
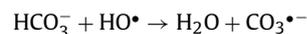


Fig. 8. Percent CBZ removal as a function of time at different alkalinities (as CaCO₃ concentration).

Table 3
Percent CBZ removal with different levels of alkalinity (CaCO₃ concentrations), after 90 min of irradiation.

% Removal	Alk. conc. (mg/L as CaCO ₃)					
	0	25	50	100	200	300
	72.6	68.5	60.6	42.4	36.8	30.3

As seen in Fig. 8, at 25 mg/L CaCO₃, there was a negligible effect of alkalinity on CBZ removal. There was a drastic decrease, however, in CBZ removal at 100 mg/L CaCO₃. Interestingly, after increasing the alkalinity to over 200 mg/L CaCO₃ there was a slow decrease in percent removal as compared to the initial decrease (Table 3). Carbonate alkalinity is known to inhibit photocatalysis efficiency in water by reacting with the generated OH[•] radicals and forming carbonate radicals (CO₃^{•-}). Reaction rates of CO₃^{•-} with organic compounds are usually several orders of magnitude lower than reaction rates of OH[•] [59,60], and therefore their influence on CBZ removal is minor.



3.9. Natural water

The CBZ-removal efficiency of sol-gel N-doped TiO₂ surfaces was tested in groundwater, surface water from Lake Kinneret, secondary effluent wastewater, and tertiary effluent wastewater after

Table 4
Water-quality analysis for different water sources.

Water type	Water quality parameter					
	pH	DOC (mg/L)	Alkalinity (mg/L as CaCO ₃)	Total hardness (mg/L as CaCO ₃)	Chlorides (mg/L Cl)	Turbidity (NTU)
Groundwater	8.1	–	224	270	80	–
Surface water	8.2	3	114	260	288	0.5
Secondary effluent	8.1	11	240	290	288	3.6
Tertiary effluent	7.3	7.5	210	260	320	0.8

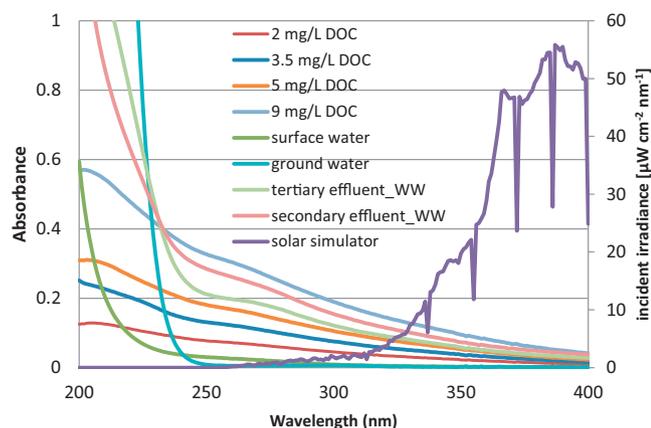


Fig. 9. Emission spectra of the solar Xe lamp and absorbance spectra of the tested waters.

in-line granular filtration with ferric chloride. The waters were passed through a 0.45- μm filter to avoid particle effects. The water-quality parameters are displayed in Table 4. Fig. 9 illustrates the absorbance of the various waters examined and the incident irradiance of the solar simulator. There is a little overlap between the water types and the solar spectrum output.

Photocatalytic degradation of CBZ decreased drastically for all types of water with average dose and time (Fig. 10a,b). CBZ removal with average dose decreased from 70% in buffered water to approximately 35%, 21% and negligible removal with surface water, groundwater and either secondary or tertiary effluent, respectively. CBZ removal with time decreased from 70% in buffered water to approximately 35%, 21% and negligible removal with surface water, groundwater and either secondary or tertiary effluent, respectively (Table 5). Apparently, CBZ removal in groundwater is lower than in surface water due to higher alkalinity values in groundwater. The reduction in average dose integrated with the water absorbance compared to DI water was 2.6% and 5.8% for surface water and secondary effluent, respectively (data not shown). The inner filter effect of NOM can be neglected in this case as well. Secondary wastewater effluents have the highest DOC value (11 mg/L, with an

alkalinity of 240 mg/L), and therefore a substantial decrease in CBZ removal rate is expected. Since numerous effects can influence CBZ removal in natural waters, it is difficult to isolate which parameters influence the photocatalytic processes separately or in synergy. Although it is obvious that pH, organic matter and alkalinity impact photocatalysis rate, other parameters not examined herein, such as metals and natural particles, might also impact adsorption to the surface and photocatalysis rate.

Only a few full-scale developments have been reported for photocatalysis in water treatment. There might be a need to improve the ratio between the catalyst's surface area and water volume to achieve enhanced removal with the photocatalytic surface. Nevertheless, these results provide a comparative perspective on the impact of water-quality parameters on sorption to surfaces and photocatalytic activity. When considering the application of photocatalytic reactors used to treat natural waters, it is important to understand the limitations of the method's efficiency with these waters. The first outdoor engineering-scale reactor developed for water treatment was a converted parabolic-trough solar thermal energy collector in which the absorber/glazing tube combination was replaced by a simple Pyrex glass tube through which contaminated water could flow [61]; a simple modification of the parabolic trough collector was then developed and successfully operated for experiments in which the catalyst was deployed in a slurry. Since that time, research all over the world has advanced a number of reactor concepts and designs, including concentrating and nonconcentrating reactors and other creative designs. The catalyst can be deployed in several ways—as a fixed catalyst, slurry, or neutral-density large particles. For example, Miranda-Garcia et al. [11] reported photocatalytic degradation of 15 emerging contaminants in municipal WWTP effluents using TiO₂ immobilized on glass spheres.

Table 5
Percent CBZ removal for different water types after 90 min of exposure.

Water type	Groundwater	Surface water	Secondary effluent	Tertiary effluent
% Removal	23.2	37.4	5.8	12.2

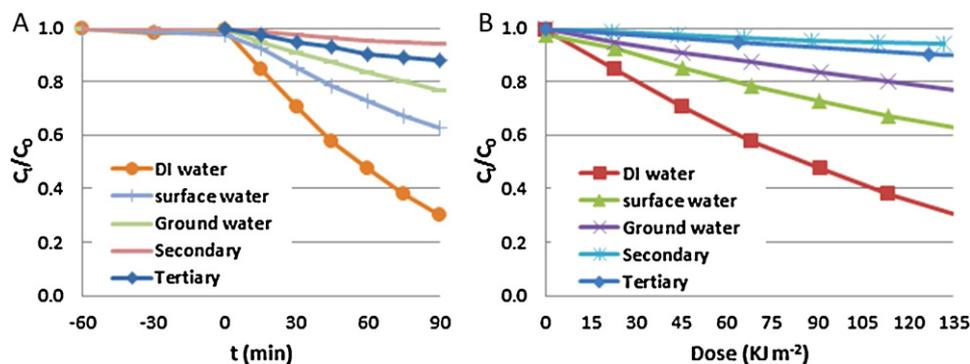


Fig. 10. Percent CBZ removal in different water sources as a function of time (a) and dose (b).

4. Conclusions

1. CBZ was stable to photodegradation under direct solar irradiation.
2. Polycrystalline N-doped TiO₂ thin films have been deposited by sol-gel dip-coating.
3. No sorption of CBZ to the N-doped TiO₂ catalyst surface was observed, as confirmed by surface characterization using XPS analysis.
4. An excess amount of C was detected compared to the control when the catalyst surface was immersed in NOM, indicating some sorption of organics to the surface.
5. The catalyst surface charge was negative at all pH values from 4 to 10 and the charge decreased with increasing pH.
6. CBZ removal improved with increasing medium pH in the range of 5–9.
7. DOC at a concentration of 5 mg/L resulted in an ~20% reduction in CBZ removal, probably due to competitive inhibition of the photocatalytic degradation of CBZ.
8. Alkalinity values of 100 mg/L as CaCO₃ resulted in an over 40% decrease in CBZ removal.
9. A 35% reduction in CBZ removal occurred in the presence of surface water compared to complete suppression of the photocatalytic process in wastewater effluent.

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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.jhazmat.2012.09.058>.

References

- [1] P.J. Sullivan, F.J. Agardy, J.J.J. Clark, *The Environmental Science of Drinking Water*, 1st ed., Elsevier Butterworth-Heinemann, Burlington, MA, 2005.
- [2] D. Avisar, Y. Lester, D. Ronen, Sulfamethoxazole detected in a deep phreatic aquifer beneath effluent irrigated land, *Sci. Total Environ.* 407 (2009) 4278–4282.
- [3] D. Avisar, G. Levin, I. Gozlan, The processes affecting oxytetracycline contamination of groundwater in a phreatic aquifer underlying industrial fish ponds in Israel, *Environ. Earth Sci.* 59 (2009) 939–945.
- [4] S. Ollers, H.P. Singer, P. Fassler, S.R. Muller, Simultaneous quantification of neutral and acidic pharmaceuticals and pesticides at the low-ng/l level in surface and waste water, *J. Chromatogr. A* 911 (2001) 225–234.
- [5] L. Rizzo, S. Meric, M. Guida, D. Kassinos, V. Belgiorno, Heterogeneous photocatalytic degradation kinetics and detoxification of an urban wastewater treatment plant effluent contaminated with pharmaceuticals, *Water Res.* 43 (2009) 4070–4078.
- [6] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69–96.
- [7] T.E. Doll, F.H. Frimmel, Removal of selected persistent organic pollutants by heterogeneous photocatalysis in water, *Catal. Today* 101 (2005) 195–202.
- [8] C. Reyes, J. Fernandez, J. Freer, M.A. Mondaca, C. Zaror, S. Malato, H.D. Mansilla, Degradation and inactivation of tetracycline by TiO₂ photocatalysis, *J. Photochem. Photobiol. A: Chem.* 184 (2006) 141–146.
- [9] L. Yang, L.E. Yu, M.B. Ray, Degradation of paracetamol in aqueous solutions by TiO₂ photocatalysis, *Water Res.* 42 (2008) 3480–3488.
- [10] E. Hapsheshi, A. Achilleos, M.I. Vasquez, C. Michael, N.P. Xekoukoulotakis, D. Mantzavinos, D. Kassinos, Drugs degrading photocatalytically: kinetics and mechanisms of ofloxacin and atenolol removal on titania suspensions, *Water Res.* 44 (2010) 1737–1746.
- [11] N. Miranda-Garcia, S. Suarez, B. Sanchez, B. Coronado, S. Malato, M.I. Maldonado, Photocatalytic degradation of emerging contaminants in municipal wastewater treatment plant effluents using immobilized TiO₂ in a solar pilot plant, *Appl. Catal. B: Environ.* 103 (2011) 294–301.
- [12] A.G. Rincon, C. Pulgarin, Bactericidal action of illuminated TiO₂ on pure *Escherichia coli* and natural bacterial consortia: post-irradiation events in the dark and assessment of the effective disinfection time, *Appl. Catal. B: Environ.* 49 (2004) 99–112.
- [13] J.C. Sjogren, R.A. Sierka, Inactivation of phage MS2 by iron-aided titanium-dioxide photocatalysis, *Appl. Environ. Microbiol.* 60 (1994) 344–347.
- [14] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, *Prog. Solid State Chem.* 32 (2004) 33–177.
- [15] C.L. Wong, Y.N. Tan, A.R. Mohamed, A review on the formation of titania nanotube photocatalysts by hydrothermal treatment, *J. Environ. Manage.* 92 (2011) 1669–1680.
- [16] C.F. Lin, C.H. Wu, Z.N. Onn, Degradation of 4-chlorophenol in TiO₂, WO₃, SnO₂, TiO₂/WO₃ and TiO₂/SnO₂ systems, *J. Hazard. Mater.* 154 (2008) 1033–1039.
- [17] C. Martinez, M. Canle, M.I. Fernandez, J.A. Santaballa, J. Faria, Kinetics and mechanism of aqueous degradation of carbamazepine by heterogeneous photocatalysis using nanocrystalline TiO₂, ZnO and multi-walled carbon nanotubes-anatase composites, *Appl. Catal. B: Environ.* 102 (2011) 563–571.
- [18] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Visible-light photocatalysis in nitrogen-doped titanium oxides, *Science* 293 (2001) 269–271.
- [19] RxList. The Internet Drug Index. <http://www.rxlist.com>, 2006.
- [20] T. Kosjek, H.R. Andersen, B. Kompere, A. Ledin, E. Heath, Fate of carbamazepine during water treatment, *Environ. Sci. Technol.* 43 (2009) 6256–6261.
- [21] Y. Zhang, S.U. Geissen, C. Gal, Carbamazepine and diclofenac: removal in wastewater treatment plants and occurrence in water bodies, *Chemosphere* 73 (2008) 1151–1161.
- [22] A. Joss, S. Zabaczynski, A. Göbel, B. Hoffmann, D. Löffler, C.S. McArdell, T.A. Ternes, A. Thomsen, H. Siegrist, Biological degradation of pharmaceuticals in municipal wastewater treatment: proposing a classification scheme, *Water Res.* 40 (2006) 1686–1696.
- [23] M. Clara, B. Strenn, N. Kreuzinger, Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behaviour of carbamazepine in wastewater treatment and during groundwater infiltration, *Water Res.* 38 (2004) 947–954.
- [24] T. Okuda, Y. Kobayashi, R. Nagao, N. Yamashita, H. Tanaka, S. Tanaka, S. Fujii, C. Konishi, I. Houwa, Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan, *Water Sci. Technol.* 57 (2008) 65–71.
- [25] R. Andreozzi, R. Marotta, G. Pinto, A. Pollio, Carbamazepine in water: persistence in the environment, ozonation treatment and preliminary assessment on algal toxicity, *Water Res.* 36 (2002) 2869–2877.
- [26] D.C. McDowell, M.M. Huber, M. Wagner, U. von Gunten, T.A. Ternes, Ozonation of carbamazepine in drinking water: identification and kinetic study of major oxidation products, *Environ. Sci. Technol.* 39 (2005) 8014–8022.
- [27] M.M. Huber, S. Canonica, G.Y. Park, U. von Gunten, Oxidation of pharmaceuticals during ozonation and advanced oxidation processes, *Environ. Sci. Technol.* 37 (2003) 1016–1024.
- [28] D. Vogna, R. Marotta, R. Andreozzi, A. Napolitano, M. d'Ischia, Kinetic and chemical assessment of the UV/H₂O₂ treatment of antiepileptic drug carbamazepine, *Chemosphere* 54 (2004) 497–505.
- [29] T.E. Doll, F.H. Frimmel, Fate of pharmaceuticals—photodegradation by simulated solar UV-light, *Chemosphere* 52 (2003) 1757–1769.
- [30] V.J. Pereira, H.S. Weinberg, K.G. Linden, P.C. Singer, UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm, *Environ. Sci. Technol.* 41 (2007) 1682–1688.
- [31] A. Achilleos, E. Hapsheshi, N.P. Xekoukoulotakis, D. Mantzavinos, D. Fatta-Kassinos, UV-A and solar photodegradation of ibuprofen and carbamazepine catalyzed by TiO₂, *Sep. Sci. Technol.* 45 (2010) 1564–1570.
- [32] J.R. Dominguez, T. Gonzalez, P. Palo, E.M. Cuerda-Correa, Fenton + fenton-like integrated process for carbamazepine degradation: optimizing the system, *Ind. Eng. Chem. Res.* 51 (2012) 2531–2538.
- [33] N. Klammerth, L. Rizzo, S. Malato, M.I. Maldonado, A. Agüera, A.R. Fernández-Alba, Degradation of fifteen emerging contaminants at microg l⁻¹ initial concentrations by mild solar photo-Fenton in MWTP effluents, *Water Res.* 44 (2010) 545–554.
- [34] R. Bianchini, L. Calucci, C. Lubello, C. Pinzino, Intermediate free radicals in the oxidations of wastewater, *Res. Chem. Intermed.* 28 (2002) 247–256.
- [35] Y. Goswami, M. Blake, Cleaning up with sunshine, *Mech. Eng.* 118 (1996) 56–60.
- [36] J. Yu, X. Zhao, J. Du, W. Chen, Preparation, microstructure and photocatalytic activity of the porous TiO₂ anatase coating by sol-gel processing, *J. Sol-Gel Sci. Technol.* 17 (2000) 163.
- [37] M. Elimelech, J. Gregory, X. Jia, R. Williams, *Particle Deposition and Aggregation: Measurement, Modeling and Simulation*, Butterworth-Heinemann, University of Michigan, 1995.
- [38] American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), *Standard Methods for the Examination of Water and Wastewater*, 21st ed., Washington, DC, 2005.
- [39] S-H. Lee, E. Yamasue, K.N. Ishihara, H. Okumura, Photocatalysis and surface doping states of N-doped TiOx films prepared by reactive sputtering with dry air, *Appl. Catal. B: Environ.* 93 (2010) 217–226.

- [40] K. Birdi, D. Vu, A. Winter, A study of the evaporation rates of small water drops placed on a solid surface, *J. Phys. Chem. A* 93 (1989) 3702–3703.
- [41] X. Zhu, C. Yuan, Y. Bao, J. Yang, Y. Wu, Photocatalytic degradation of pesticide pyridaben on TiO₂ particles, *J. Mol. Catal. A: Chem.* 229 (2005) 95–105.
- [42] S. Castiglioni, R. Bagnati, R. Fanelli, F. Pomati, D. Calamari, E. Zuccato, Removal of pharmaceuticals in sewage treatment plants in Italy, *Environ. Sci. Technol.* 40 (2006) 357–363.
- [43] X.S. Miao, J.J. Yang, C.D. Metcalfe, Carbamazepine and its metabolites in wastewater and in biosolids in a municipal wastewater treatment plant, *Environ. Sci. Technol.* 39 (2005) 7469–7475.
- [44] T. Reemtsma, S. Weiss, J. Mueller, M. Petrovic, S. Gonzalez, D. Barcelo, F. Ventura, T.P. Knepper, Polar pollutants entry into the water cycle by municipal wastewater: a European perspective, *Environ. Sci. Technol.* 40 (2006) 5451–5458.
- [45] L. Dsikowitzky, J. Schwarzbauer, R. Littke, The anthropogenic contribution to the organic load of the Lippe River (Germany). Part II. Quantification of specific organic contaminants, *Chemosphere* 57 (2004) 1289–1300.
- [46] C. Tixier, H.P. Singer, S. Oellers, S.R. Muller, Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters, *Environ. Sci. Technol.* 37 (2003) 1061–1068.
- [47] S. Wiegel, A. Aulinger, R. Brockmeyer, H. Harms, J. Löffler, H. Reincke, R. Schmidt, B. Stachel, W. von Tumpling, A. Wanke, Pharmaceuticals in the river Elbe and its tributaries, *Chemosphere* 57 (2004) 107–126.
- [48] R. Fenz, A.P. Blaschke, M. Clara, H. Kroiss, D. Mascher, M. Zessner, Quantification of sewer exfiltration using the anti-epileptic drug carbamazepine as marker species for wastewater, *Water Sci. Technol.* 52 (2005) 209–217.
- [49] T.J. Scheytt, P. Mersmann, T. Heberer, Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments, *J. Contam. Hydrol.* 83 (2006) 53–69.
- [50] J.E. Drewes, T. Heberer, T. Rauch, K. Reddersen, Fate of pharmaceuticals during ground water recharge, *Ground Water Monit. Rem.* 23 (2003) 64–72.
- [51] T. Heberer, A. Mechlinski, B. Fanck, A. Knappe, G. Massmann, A. Pekdeger, B. Fritz, Field studies on the fate and transport of pharmaceutical residues in bank filtration, *Ground Water Monit. Rem.* 24 (2004) 70–77.
- [52] M. Kahle, I.J. Buerge, M.D. Muller, T. Poiger, Hydrophilic anthropogenic markers for quantification of wastewater contamination in ground- and surface waters, *Environ. Toxicol. Chem.* 28 (2009) 2528–2536.
- [53] V. Matamoros, A. Duhec, J. Albaiges, J. Bayona, Photodegradation of carbamazepine, ibuprofen, ketoprofen and 17 α -ethinylestradiol in fresh and seawater, *Water Air Soil Pollut.* 196 (2009) 161–168.
- [54] T.A. Ternes, M. Meisenheimer, D. McDowell, F. Sacher, H.J. Brauch, B. Haist-Gulde, G. Preuss, U. Wilme, N. Zulei-Seibert, Removal of pharmaceuticals during drinking water treatment, *Environ. Sci. Technol.* 36 (2002) 3855–3863.
- [55] R.W. Mathews, Photooxidation of organic material in aqueous suspensions of titanium dioxide, *Water Res.* 20 (1986) 569–578.
- [56] C. Shifu, C. Gengyu, Photocatalytic degradation of pesticides using floating photocatalyst TiO₂-SiO₂ beads by sunlight, *Solar Energy* 79 (2005) 1–9.
- [57] K. Selvam, M. Muruganandham, I. Muthuvel, M. Swaminathan, The influence of inorganic oxidants and metal ions on semiconductor sensitized photodegradation of 4-fluorophenol, *Chem. Eng. J.* 128 (2007) 51–57.
- [58] T.E. Doll, F.H. Frimmel, Photocatalytic degradation of carbamazepine, clofibric acid and iomeprol with P25 and Hombikat UV100 in the presence of natural organic matter (NOM) and other organic water constituents, *Water Res.* 39 (2005) 403–411.
- [59] D.S. Bhatkhande, V.G. Pangarkar, A.A. Beenackers, Photocatalytic degradation for environmental applications—a review, *J. Chem. Technol. Biotechnol.* 77 (2002) 102–116.
- [60] J.P. Huang, S.A. Mabury, A new method for measuring carbonate radical reactivity toward pesticides, *Environ. Toxicol.* 19 (2000) 1501–1507.
- [61] D.Y. Goswami, D.M. Blake, Cleaning up with sunshine, *Mech. Eng.* 118 (1996) 56–59.