

Removal of hazardous pharmaceutical from water by photocatalytic treatment

Research Article

J. Choina^{a,b}, H. Duwensee^d, G.-U. Flechsig^d, H. Kosslick^{b,c},
A.W. Morawski^a, V.A Tuan^e and A. Schulz^{*,b,c}

^aWest Pomerania University of Technology, Department of Water Technology and Environment Engineering, Institute of Chemical and Environment Engineering, 70-322 Szczecin, Poland

^bUniversity of Rostock, Institute of Chemistry, Department of Inorganic Chemistry, Rostock, Germany

^cLeibniz Institute of Catalysis e.V. (LIKAT), Rostock, Germany

^dUniversity of Rostock, Institute of Chemistry, Department of Analytical, Technical and Environmental Chemistry, Rostock, Germany

^eVietnamese Academy of Science and Technology, Institute of Chemistry, Cau Giay, Hanoi, Vietnam

Received 17 May 2010; Accepted 25 August 2010

Abstract: The photocatalytic abatement of hazardous pharmaceuticals has been investigated at very low concentration in the ppb range as found in wastewater and in environmental pollutants. Photocatalytic degradation of tetracycline as a model compound with titania catalysts has been studied using solarium UV-A and black light with differentially applied electric power, tetracycline and catalyst concentration. Abatement of up to 90% has been achieved after 1 hour. Adsorption of tetracycline and photochemical degradation contribute significantly to the abatement of tetracycline resulting in an immediate reduction during the initial period of treatment. Contribution of adsorption is high at very low concentration (500 ppb). Photocatalytic treatment with titania is even highly efficient in the abatement of very small concentrations of tetracycline in drinking water.

Keywords: Photocatalysis • Titania • Cyclic voltammetry • Tetracycline abatement • Low concentration ppb range

© Versita Sp. z o.o.

1. Introduction

Water contamination with small concentrations of pollutants such as pharmaceuticals, hormones, and pesticide are a serious problem [1-4]. Pharmaceuticals are now attracting attention as a potentially new class of water pollutant. Such drugs as antibiotics, antidepressants, birth control pills, seizure medicines, cancer treatments, pain killers, tranquilizers and cholesterol-lowering compounds have been detected in varied water sources [5-8]. They may be extremely dangerous for the environment because they are able to perform adverse biological effects on living organisms, sometimes in a non-predictable manner. Pharmaceutical industries, hospitals

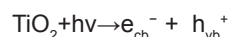
and other medical facilities are obvious sources. But households, agriculture and fish farming also contribute a significant share. People often dispose of unused medicines by flushing them down toilets, and human excreta can contain various incompletely metabolized agents. In the environment, pharmaceuticals have been detected in hospital wastewaters [9], in surface water such as rivers and lakes [10], in marine waters [11] as well as in soil matrices [12]. Recent investigations have shown that a number of biological compounds are not completely eliminated in wastewater treatment and are also not biodegradable. Many pollutants are present in very low concentrations within the lower ng L⁻¹ scale [13]. Some active compounds possess an extremely high biological potency down to doses in the range of

* E-mail: axel.schulz@uni-rostock.de

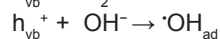
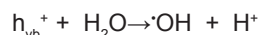
$\mu\text{g day}^{-1}$. Therefore, concentrations, which are as low as 1 ng L^{-1} can be dangerous. Complete decomposition of these hazardous compounds is very important [14-16].

New wastewater purification technology leading to the complete mineralization of organic pollutants is now considered the most suitable solution concerning the contamination level in water and wastewater. Recently, advanced oxidation processes (AOPs) have been proposed as an alternative method for water purification [17]. AOPs have achieved ca. 60% degradation of pollutants and 90% with additional filtration over active carbon [2]. However, they often require the use of expensive reactants such as H_2O_2 or O_3 and, therefore, it is obvious that these applications should be replaced [18]. Besides these processes, photocatalysis can play an important role in new technologies of water and wastewater purification. As a major photocatalyst, titania is active in water purification by photocatalytic decomposition of organic pollutants in water [19].

The basic process of photocatalysis consists of exciting an electron from the valence band (VB) to the conduction band (CB) of the TiO_2 semi-conductor creating a h^+ hole in the valence band. This is due to UV irradiation of TiO_2 with an energy equal or superior to the band gap ($>3.2 \text{ eV}$):



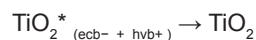
This is followed by formation of extremely reactive radicals (like $\cdot\text{OH}$) at the semi-conductor surface and/or a direct oxidation of the polluting species (R):



The excited electrons react with electron acceptors such as oxygen adsorbed or dissolved in water:



Also, the electrons and holes present in activated TiO_2^* can occur by internal recombination.



Photocatalytic reactions are one of the most promising technologies for eliminating organic micro-pollutants because they are highly efficient and can degrade contaminants under different energy sources [20]. Photocatalytic decomposition of organics assisted by heterogeneous catalysts based on titania is very attractive; it is a green process and addition of chemicals

is avoided. Titania is a non-hazardous compound, and it promotes eco-friendly decomposition of hazardous organics in water. Titania can also be recovered and reused. From a technological point of view, titanium dioxide acts as a deodorizer, self-cleaner and a bactericidal. In principle, titania can also be used in water treatment without any additional methods such as various biological and chemical processes [21].

For the abatement of hazardous compounds like pharmaceuticals, information about the photocatalytic performance of titania at very low concentrations, down to the low ppb or ppt range, is needed. However, most investigators report using higher concentrated solutions and large amounts of catalysts. In order to simulate sewage water conditions, they are mainly dedicated to the treatment of highly contaminated wastewater. Therefore, usually large amounts of pollutants in the mg L^{-1} to g L^{-1} scales are used ($20\text{-}50 \text{ mg L}^{-1}$). In contrast, contaminations with low concentrations are of greater interest because low concentrations of biologically active components may have serious effects [22]. Furthermore, large amounts of catalysts are added to detect photocatalytic activity between $0.1 - 2 \text{ g L}^{-1}$ [23,24]. Investigations at very low concentrations require the development of appropriate analytical protocols for the determination of very low amounts of contaminant in water.

In this work, tetracycline, representing an important family of antibiotics, has been chosen as a model compound for the investigation of the photo-catalytic disruption of low concentrated pollutants by different catalysts and conditions. We have shown that titania is an efficient catalyst for the abatement of very small amounts of pharmaceuticals in waste and drinking water. Therefore, photo-catalytic investigation was undertaken without additional chemicals. Low concentrated aqueous tetracycline solutions were slightly acidic. Depending on the pH of the solution, tetracycline is present in different protonated states. Under acidic conditions

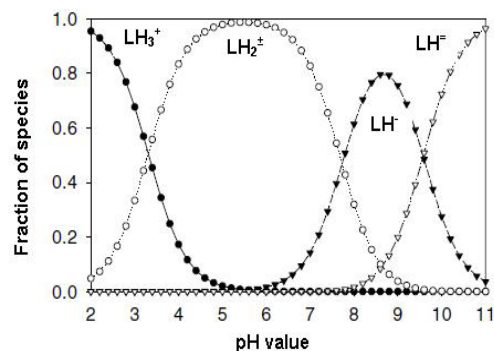


Figure 1. Influence of the pH value on the distribution of tetracycline species in aqueous solution after [26].

(pH= 4 - 7), as considered in this report, the zwitterionic form dominates (LH_2^+) as shown in Fig. 1 [25-28].

An extremely sensitive electrochemical procedure for trace tetracycline detection has been developed in order to follow the effect of the catalytic treatment efficiently. Adsorptive accumulation coupled with differential pulse voltammetry allows the determination of very low compound concentrations in aqueous solution [29,30]. The cyclic voltammetry technique is of general importance to quantitatively follow the degradation of hazardous compounds at low concentration by adsorption and photo-catalysis [31].

2. Experimental Procedure

2.1. Materials

Tetracycline (TC) 95% ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8 \cdot \text{HCl}$) was purchased from Sigma. Tetracycline's structure is presented in Fig. 2.

Degussa P25 titanium dioxide was used as a photo-catalyst. This material has a specific surface area of ca. $50 \text{ m}^2 \text{ g}^{-1}$ and is composed of 80% anatase and 20% rutile [32]. The P25 catalyst is nanocrystalline as show by the TEM image in Fig. 3. For comparison, sol-gel prepared titania and zirconium-titania catalysts were included. The effect of nitrogen and iron doping on the catalytic performance has been inspected. Highly disperse titania catalysts were prepared by sol-gel synthesis combined with hydrothermal treatment. A determined amount of TiCl_4 was added drop wise into i-propanol. The resulting solution was introduced into distilled water in an ice-water bath with vigorous magnetic stirring. After that, the pH value of this acidic solution was adjusted to 7 by adding an NH_4OH solution to form a white gel. The resulting gel was aged for 24 h at room temperature with continuous stirring. The resulting white precipitate was filtered and washed repeatedly with distilled water until complete removal of chloride ion. Thereafter, the precipitate was well dispersed by treating in an ultrasonic bath. 30% H_2O_2 was added drop wise into this mixture while stirring. The resulting yellow transparent solution was poured into an autoclave and heated at 100°C for 20 h. After the hydrothermal treatment, the precipitate was washed and dried at 100°C . As a result, a highly dispersed TiO_2 powder was obtained. Prior to further use, titania was calcined at 400°C .

The TEM image shows that these materials consist of inter-grown nanoparticles (Fig. 4). The specific surface area of sol gel-prepared and calcined materials is ca. $180 \text{ m}^2 \text{ g}^{-1}$. The XRD patterns show that sol-gel derived TiO_2 were crystalline and belong to the anatase crystal

structure (Fig. 5). The specific surface area was ca. $240 \text{ m}^2 \text{ g}^{-1}$. Doping with elements did not markedly influence the crystal structure and texture, which may be due to the low concentration used.

Doping of sol-gel derived titania with nitrogen and zirconium was carried out by in situ crystallization. Appropriate amounts of urea and zirconium i-propoxide were added to the starting TiCl_4 i-propanol solution. Due to the high precipitation tendency of iron hydroxide,

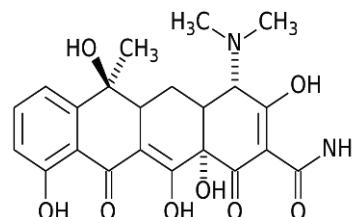


Figure 2. Structure of tetracycline.

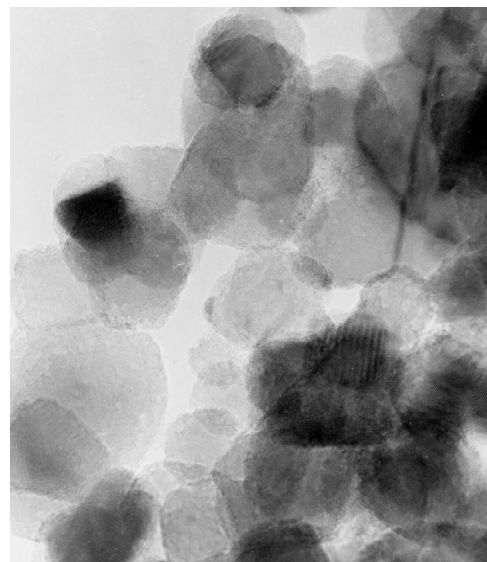


Figure 3. TEM image of the commercial titania P25 photocatalyst (Degussa) showing particles with sizes ranging from 10 to 40 nm.

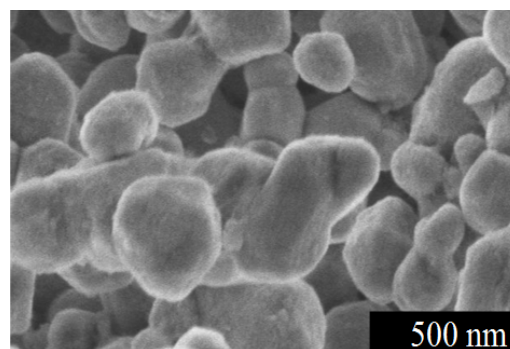


Figure 4. TEM image of titania obtained by sol-gel synthesis calcined at 400°C with particle sizes ranging from 100 to 250 nm.

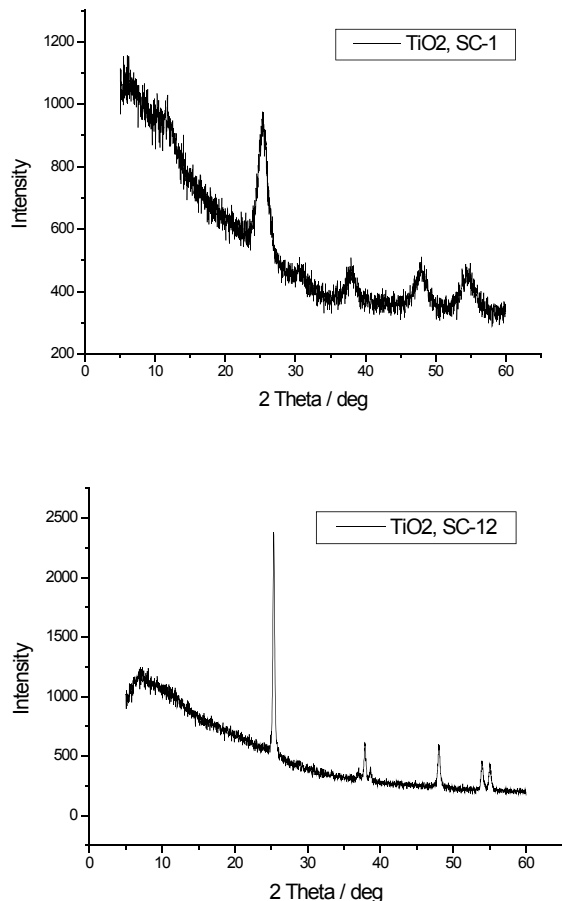


Figure 5. XRD patterns of sol-gel TiO_2 (anatase) after hydrothermal treatment for 1 h at 100°C (top) and after calcinations at 400°C (below).

the iron doping was carried out by chemical vapour deposition (CVD) using FeCl_3 as the metal source. CVD doping was carried out in a $2\text{ cm} \times 25\text{ cm}$ quartz tube reactor. A determined amount of FeCl_3 and pre-calcined titania, separated by quartz wool, were placed into the reactor and heated to 350°C under nitrogen flow first passing the metal source. The heating rate was 10 K min^{-1} . The temperature was held at 350°C for 30 minutes. Thereafter, direction of the gas flow was changed in order to remove excess iron chloride from the surface of the titania. The reactor was then allowed to cool down to remove the catalyst.

2.2. Characterization

The chemical composition was determined by ICP analysis. Electron micrographic images were recorded on a Field Emission Scanning Electron Microscope, Hitachi S-4800). The XRD patterns were recorded on a Siemens D5000 XRD spectrometer. Textural properties

were investigated by nitrogen adsorption-desorption isotherm measurements using a Micromeritics ASAP device.

2.3. Chemical analysis

The degradation processes were monitored by measuring the change of the tetracycline concentration by means of a 797 VA Computrace polarograph (Metrohm AG, Herisau, Switzerland). To detect traces of this analyte, adsorptive stripping voltammetry (AdSV) was performed using the following parameters: 180 s deposition at -0.6 V under stirring (2000 rpm) at the hanging mercury drop electrode (HMDE) followed by a differential pulse voltammetric scan (50 mV pulses) from -0.4 to -1.6 V (vs. $\text{Ag}/\text{AgCl}/3\text{ M KCl}$). Under these experimental conditions, only the tetracycline peak is observed. All solutions were prepared using ultrapure water ($> 18\text{ M } \Omega\text{ cm TOC} < 2\text{ ppb}$). A stock solution (100 ppm) of tetracycline (Sigma) was prepared daily. A 0.025 M boric acid solution, adjusted to pH 5.5, was used as a supporting electrolyte.

For the analysis, 10 mL of each of the supporting electrolyte solution and the tetracycline sample were pipetted into the cell and deoxygenated with nitrogen for 300 seconds. Each AdSV measurement was repeated once in the same sample using a fresh Hg drop. All data were obtained at room temperature.

2.4. Photocatalytic testing

For photocatalytic investigations two types of irradiation were used: solarium device UV-A light lamps (15 W, Phillips) and black light lamps (8 W, Phillips). Decomposition of tetracycline (initial concentration ca. 500 ppb, 1 ppm or 2 ppm) was carried out in an aluminum closed box, equipped with a UV-A or black lamp and a glass beaker of ca. 800 mL size filled with 600 mL of the reaction solution (Fig. 6). The distance between applied lamps and the surface of the tetracycline solution was 15 cm. All tetracycline abatement tests were taken to the same concentration of catalyst (0.002 g L^{-1}). The pH value of the starting solutions containing tetracycline and catalyst was ca. 5.4. The pH did not change markedly during the experiment because of the very low concentration of the tetracycline and titania catalyst. The solution was magnetically stirred during adsorption and photocatalytic treatment. The catalysts were separated from the aqueous solution by means of a centrifugal clarifier. Additionally, control measurements were carried out in the dark in order to check the contribution of adsorption.

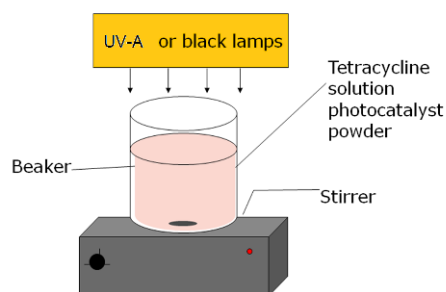


Figure 6. Photocatalytic setup.

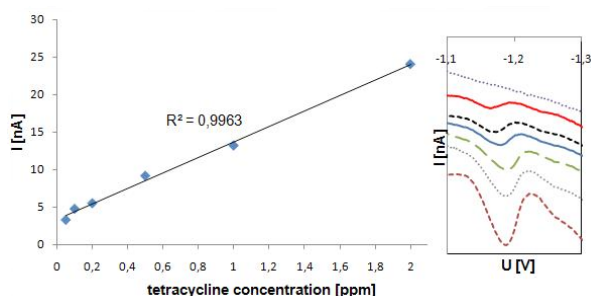


Figure 7. Calibration plot (left) and adsorptive stripping voltammetric response (right) of 0, 0.05, 0.1, 0.2, 0.5, 1 and 2 ppm aqueous tetracycline solution (from top to bottom) in 25 mM boric acid (pH 5.5), deposition time: 180 s, deposition potential: 600 mV.

3. Results and Discussions

Analysis of tetracycline abatement from aqueous solution was monitored by adsorptive stripping voltammetry (AdSV). The measurements were carried out in boric acid solution [31]. In each case, the complete experiments (photocatalytic and adsorptive abatement of TC, and analytical measurements) were repeated twice.

Fig. 7 depicts AdSV calibration data obtained with tetracycline in the range of 0 to 2 ppm. A <10 ppb detection limit can be estimated based on the signal-to-noise characteristics of a sample at this TC concentration (data not shown). Our calibration experiments indicate that TC concentrations can be easily determined down to the low ppb-level by means of AdSV at the HMDE. The influence of different photocatalysts, the commercial P25 (TiO_2 -P25), the nitrogen (N- TiO_2), iron (Fe- TiO_2) and zirconium (Zr- TiO_2) modified titania on the abatement of tetracycline, has been investigated. Additionally, different light sources, a UV-A lamp (solarium device) and black light, have been used to check the influence of the spectral composition of radiation on the catalytic performance. For comparison, blank irradiation tests in the absence of the catalyst were carried out in order to check for a possible contribution of photochemical degradation alone. Formation of reactive radicals may occur under UV-A irradiation leading to abatement of

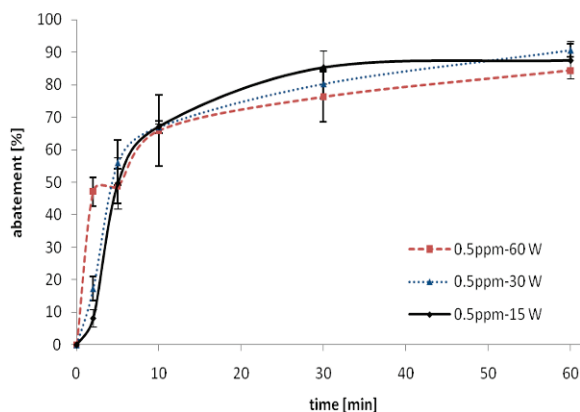


Figure 8. Photocatalytic assisted abatement of tetracycline (500 ppb) under UV-A radiation by using photocatalysts TiO_2 -P25: UV-A 60 W (red curve), UV-A 30 W (blue curve), UV-A 15 W (black curve).

organic pollutants. Under the present experimental condition, degradation of TC by irradiation linearly increases. After 60 min of treatment ca. 10% of TC is degraded. In contrast, rapid tetracycline degradation is observed already in the presence of very small amounts of 0.002 g L^{-1} of catalyst (Fig. 8). An initial period of fast abatement up to ca. 10 min is followed by a second period with markedly lower abatement. After 60 min, the concentration of TC decreased by ca. 90%. Hence, the photocatalytic abatement of pollutants by titania catalysts is of very high efficiency.

Fig. 8 presents the influence of the applied electric power on the photo-catalytical assisted abatement of tetracycline. For this UV-A lamps with different electric powers of 15, 30, 60 W were used. At the low pollutant concentration of 500 ppb, increase of electric power has no impact on the abatement. Obviously, low pollutant concentration requires weak radiation power.

Additional abatement experiments have been carried out, in order to check the sensitivity of the photocatalytic system against changes of concentration and radiation power. With increasing pollutant concentration from 0.5 ppm to 1 ppm, some effect of the electric power of the abatement is observed. Considering Fig. 9, abatement increases with the electric power from 15 to 60 W. After 60 min of treatment, abatements of 75% and 90% have been achieved.

With further increases of TC concentration to 2 ppm of tetracycline solution per 2 mg titania, the catalyst achieved relative abatement decreases. With larger amounts of contaminants in the water, the activity of photocatalytic decomposition is maintained. In both cases, the same absolute amount of pollutant is removed. After 60 min of radiation, results showed a 50% removal of pollutants under a 15 W lamp and 70% under a 60 W lamp (Fig. 10). Taking into account the increased contribution of photochemical degradation,

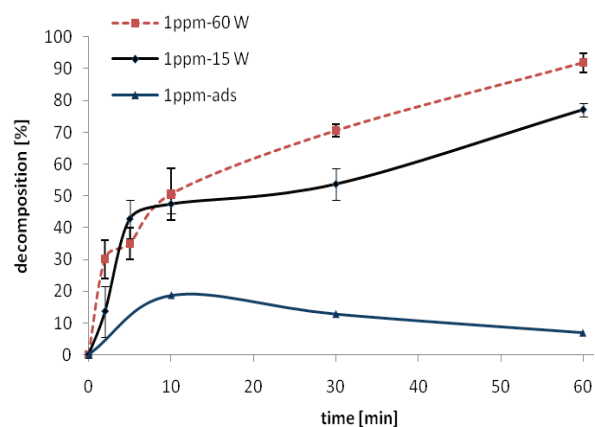


Figure 9. Photocatalytic assisted abatement of tetracycline (1 ppm) under UV-A radiation by using photocatalysts $\text{TiO}_2\text{-P25}$: UV-A 60 W (above red curve), UV-A 15 W (middle black curve), adsorption (below blue curve).

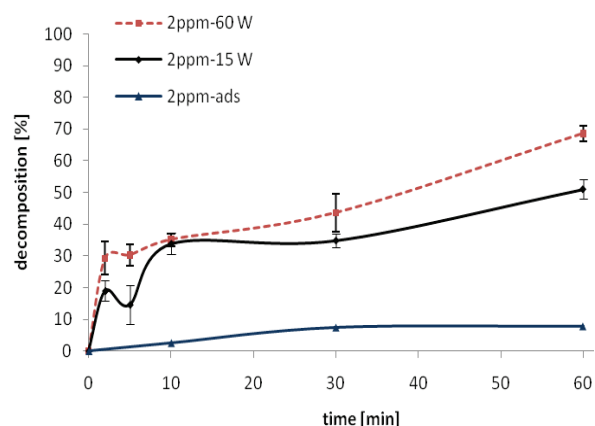


Figure 10. Photocatalytic assisted abatement of tetracycline (2 ppm) under UV-A radiation by using photocatalysts $\text{TiO}_2\text{-P25}$: UV-A 60 W (above red curve), UV-A 15 W (middle black curve), adsorption (below blue curve).

the efficiency is slightly improved due to more efficient use of the catalyst. The system is less sensitive in the ppb concentration range. It can be concluded, however, that fast abatement of medium to higher tetracycline concentrations in water requires longer radiation time or higher catalyst concentration.

The influence of the spectral range of irradiation by different lamps was investigated using the UV-A and black light lamp. Significant decomposition (about 67%) was obtained if the black light was used in the photocatalysis process (Fig. 11). However, it is less efficient than with UV-A radiation (90%). The lower photocatalytic activity achieved with black light, radiating at 360 nm, may be due to a lower excitation efficiency of electrons from the valence to the conduction band. The energy of the 360 nm radiation is higher than the band gap of titania of 3.2 eV, which requires only 386 nm radiation. The transition probability of electrons might decrease.

In a couple of experimental runs, irregular course of abatement is observed in the initial period of catalytic

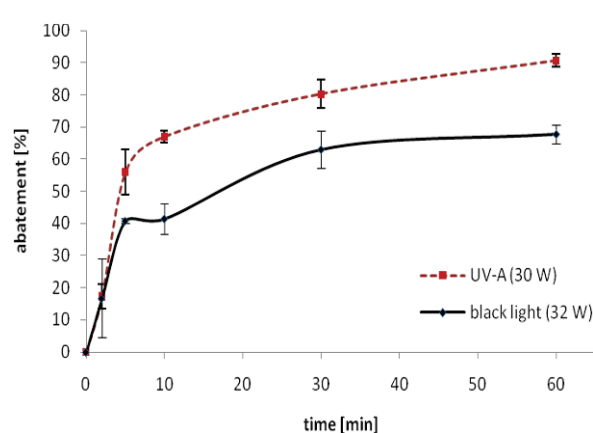


Figure 11. Photocatalytic assisted abatement of tetracycline (500 ppb) by using photocatalysts $\text{TiO}_2\text{-P25}$: under UV-A 30 W (above red curve), black light 32 W (below black curve).

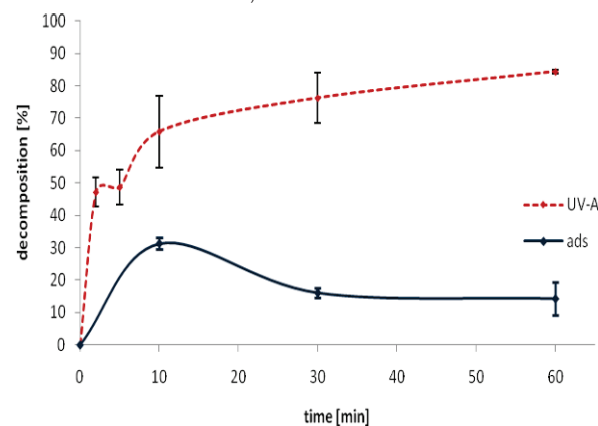


Figure 12. Photocatalytic assisted abatement of tetracycline (500 ppb, 60 W UV-A; 2 mg L^{-1} $\text{TiO}_2\text{-P25}$) above red curve, contribution of adsorption below blue curve.

treatment (compare Figs. 9, 10 and 12). These unusual changes, characterized by intermediate increase and decrease of the abatement during the treatment, are real. They might be due to inhomogeneity in the catalytic material, e.g. different strong agglomerated parts of titania catalyst. These inhomogeneities become apparent if very small amounts of catalysts (2 mg L^{-1} samples) are used. These effects are averaged by use of a larger amount. Therefore, dispersion of TiO_2 influences the tetracycline abatement. The agglomeration of catalysts and tetracycline may affect adsorption and photocatalysis. In each case, adsorption is of importance initially. During longer treatment, the contribution of photocatalysis increases. In Fig. 12, the abatement of tetracycline with very low initial concentration during the course of photocatalytic treatment with titania is shown. For comparison, the effect of adsorption (dark experiment) is shown. In the first 10 minutes, high abatement of tetracycline in aqueous solution is observed. After 10 min, 65% of TC is removed from solution. Thereafter,

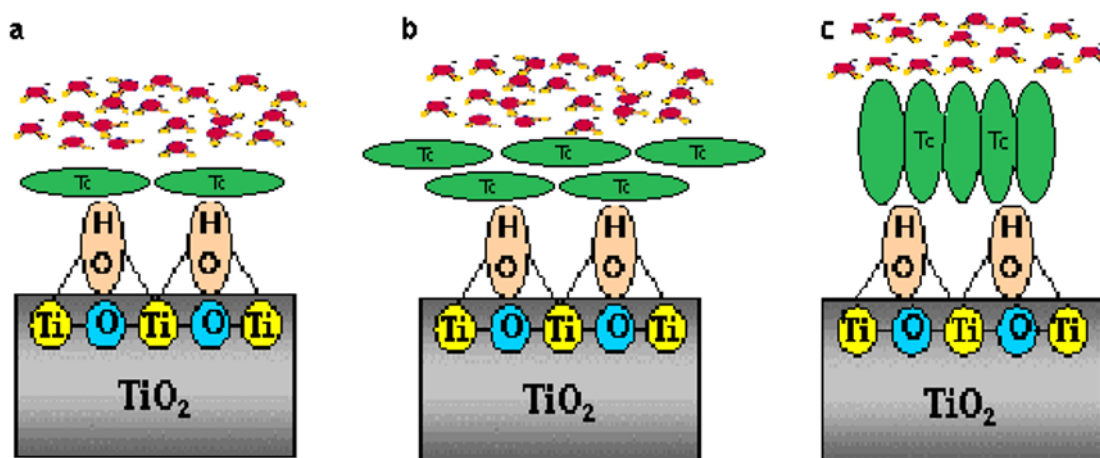


Figure 13. Scheme of the kind of adsorption of tetracycline from water on the surface of titania, (a) monolayer, (b) layer-by-layer and (c) vertically assembled.

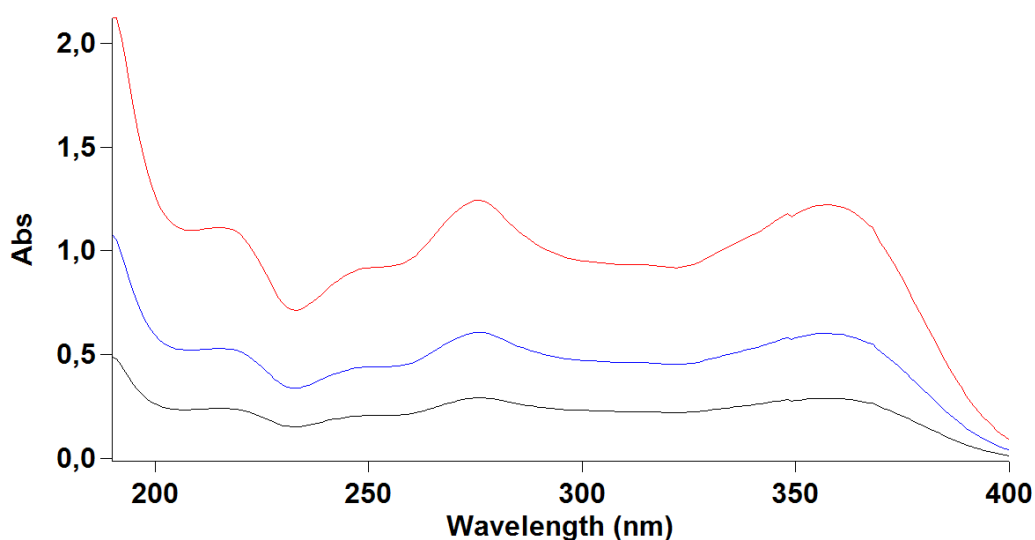


Figure 14. UV-Vis absorption spectra of tetracycline in different concentrated aqueous solutions: 40, 20, 10 ppm showing pH values of 4.1, 4.4, 4.8, respectively (from top to bottom).

the abatement proceeds much slower and reaches nearly 90% after 60 min of treatment. The comparison with the adsorption curve (dark experiment) shows strong adsorption of TC during the first steps of treatment. After 10 min, ca. 30% of TC is adsorbed. This result means adsorption contributes markedly to the abatement of TC at the first period of photocatalytic treatment. This is one reason for the fast reduction of TC concentration in wastewater at the beginning of the photocatalytic treatment at low pollutant concentration. With increasing pollutant concentration of 1 ppm and 2 ppm (Figs. 9 and 10) the relative contribution of adsorption decreases due to low catalyst concentration of 2 mg. The pH value is nearly unchanged and varies between 5.4 and 5.3. With further treatment time, photocatalytic degradation

is the dominating process for TC abatement.

Indeed, the observed tetracycline up-takes of up to 90 μg per mg of catalyst exceeds the estimated monolayer coverage of tetracycline on P25 of ca. 15 $\mu\text{g}_{\text{TC}}/\text{mg}_{\text{catalyst}}$ (assuming a molecule size of ca. $10 \times 25 \text{ \AA}$). Higher up-takes can be obtained by multilayer adsorption or a vertical arrangement of molecules in the monolayer similar to a Langmuir-Blodgett assembly (Fig. 13).

Interestingly, the loading in the low concentration range is higher than in concentrated acidic wastewater solutions [20]. The up-take decreases to 0.8 $\mu\text{g L}^{-1}$ for a solution concentration of 40 ppm TC and 500 mg L^{-1} catalyst. UV-Vis spectra of different concentrated TC solutions are shown in Fig. 14.

Table 1. Photocatalytic abatement of low concentrated tetracycline with different titania catalysts under UVA radiation.

Catalyst	Abatement of tetracycline during treatment*			
	After 10 min		After 60 min	
	Adsorption [%]**	Total [%]	Adsorption [%]**	Total [%]
N-TiO ₂	18	25	45	53
Fe-TiO ₂ ***	16	45	42	52
Zr-TiO ₂ ****	38	48	46	69
P25	31	65	15	82

*500 ppb tetracycline, 2 mg of catalyst, 60W UV-A radiation under stirring at r. t. in an open glass baker, 600 mL solution in water

**determined under the same conditions in a separate dark experiment

***0.12 ma-% Fe

****0.2 ma-% Zr

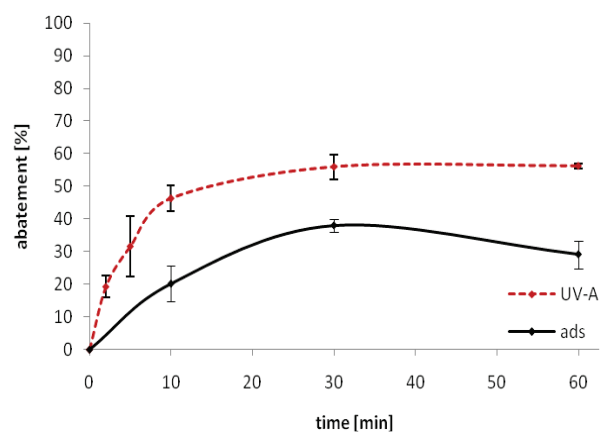


Figure 15. Photocatalytic assisted abatement of tetracycline (500 ppb, 60 W UV-A, 2 mg L⁻¹ N-TiO₂) above red curve, contribution of adsorption below black curve.

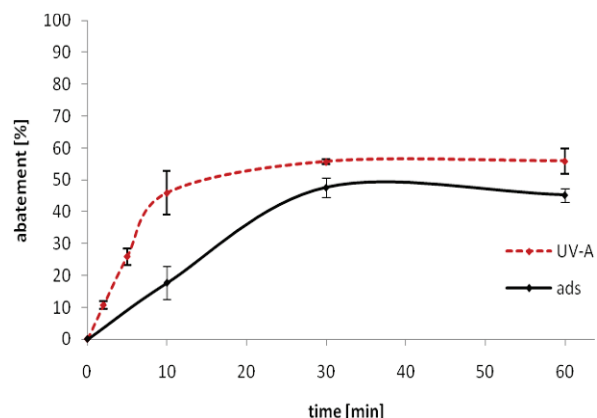


Figure 16. Photocatalytic assisted abatement of tetracycline under UV-A radiation by using iron modified TiO₂ photocatalysts Fe-TiO₂ (above red curve), contribution of adsorption to the abatement (below black curve).

They are sensitive to the degree of protonation. The position of the characteristic absorbance maximum at $\lambda_{\max}=361$ nm is not markedly changed in pH ranges between 4 and 7. It is in agreement with a zwitterionic state of tetracycline [28]. Although the nature of TC at this pH is still under discussion [33], the UV-Vis spectra confirm that the state of TC is not changed in the considered pH range. The isoelectric point of titania P25 is ca. 7.3. Therefore, titania is positively charged in the considered pH range [34] and slightly more positive

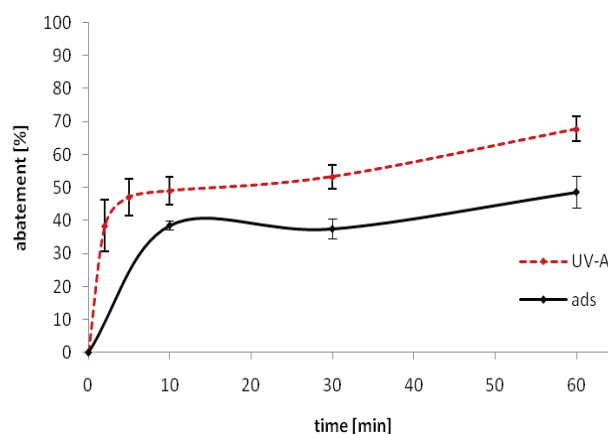


Figure 17. Photocatalytic assisted abatement of tetracycline under UV-A radiation by using zirconium modified TiO₂ photocatalysts Zr-TiO₂ (upper red curve), contribution of adsorption to the abatement (below black curve).

at stronger acidic conditions [34]. It might be that the markedly lower loading at high TC concentration is due to an increased electrostatic repulsion between the surface and the TC due to protonation combined with a competing agglomeration tendency of the tetracycline. Abatement properties of low and high concentrated solutions differ.

The abatement properties of different sol-gel catalysts are shown in Figs. 15, 16 and 17. Generally, high abatement is observed at the beginning of photocatalytic treatment. In this initial period, photocatalytic degradation contributes significantly to the abatement. Adsorption on the catalysts also occurs as seen by the dark experiments. Further prolongation of the treatment enhances the abatement slightly in the case of N-TiO₂ and Fe-TiO₂ (Figs. 15 and 16). At longer treatment time, from 30 to 60 min, the concentration of TC is not further decreased. Samples exhibit some photocatalytic activity as evidenced by decreasing contribution of adsorption. It is concluded that adsorbed TC molecules block photocatalytic active sides of sol-gel derived catalysts. The contributions of the adsorption to the abatement are larger with sol-gel derived titania catalysts than with the fumed TiO₂-P25. This may be due to high specific surface area of these catalysts. Only zirconia modified

titania catalysts show photocatalytic activity at longer treatment times leading to a total abatement of TC by ca. 70% after 60 min of treatment (Fig. 17).

In summary, all catalyst under consideration show significant abatement of tetracycline from aqueous solution after a short time of photocatalytic treatment with UV-A light of 10 minutes (Table 1).

The commercial titania P25 catalyst shows the highest abatement and highest photocatalytic activity. After longer treatment time (60 min), a further increase of abatement is observed. With P25 catalyst, a total abatement of 82% is found with major contribution from photocatalysis. The relative low contribution of adsorption could be due to high temperature treatment of the material in the flame pyrolysis process. The P25 is more ceramic in nature compared to more surface rich sol-gel materials. Sol-gel derived titania catalysts are less active. In contrast to P25, adsorption contributes mainly to the observed abatement of tetracycline. On the other hand, adsorbed molecules diminish the photocatalytic formation of active radicals. Probably the strong adsorption property of sol-gel materials is one reason for the lower photocatalytic performance of sol-gel titania. Zirconium modification has a pronounced impact on the catalytic performance of sol-gel titania catalysts. The nature of high activity of P25 is not fully understood. Low adsorption in long time treatment is obviously due to photocatalytic disruption of

adsorbed species on P25. The main difference between the commercial catalyst P25 and self-synthesized materials are the specific surface area and the phase composition. The commercial P25 catalyst consists of a mixture of anatase and rutile, whereas sol-gel derived catalysts consist of anatase. Additionally, P25 contains an amount of residual chlorine from the $TiCl_4$ flame pyrolysis process.

4. Conclusions

Photocatalysis with titania is a very efficient tool for the abatement of small concentrations of pharmaceuticals in wastewater with low amounts of catalyst. Photocatalytical investigations have been extended to very low concentration reaching the ppb scale. Additionally, the amount of catalysts could be decreased markedly to 2 mg L^{-1} . The antibiotic tetracycline has been used as a model compound for a real pharmaceutical system. The results show that a very small amount of pharmaceutical present in wastewater can be detected by adsorptive stripping voltammetry and the abatement process can be monitored effectively. In detail, the results show that adsorption contributes to the abatement in the ppb concentration range. The adsorption is more pronounced on sol-gel derived catalysts, where active sites seem to

References

- [1] D. Kolpin, E. Furlong, M. Meyer, E. Thurman, *Environ. Sci. Technol.* 36, 1202 (2002)
- [2] M.P. Ormad, N. Miguel, A. Claver, J.M. Matesanz, J.L. Ovelleiro, *Chemosphere* 71, 97 (2008)
- [3] J. Muff, Ch.D. Andersen, R. Erichsen, E.G. Soegaard, *Electrochimica Acta* 54, 2062 (2009)
- [4] A. Vidal, A.I. Díaz, A. El Hraiki, M. Romero, I. Muguruza, F. Senhaji, J. González, *Catal. Today* 54, 283 (1999)
- [5] F. Mendez-Arriaga, R.A. Torres-Palma, C. Petrier, S. Esplugas, J. Gimenez, C. Pulgarin, *Water Research* 42, 4243 (2008)
- [6] P. Mazellier, L. Méité, J. De Laat, *Chemosphere* 73, 1216 (2008)
- [7] L. Yanga, L.E. Yua, M.B. Ray, *Water Research* 42, 3480 (2008)
- [8] M.M. Huber, S. Korhonen, T.A. Ternes, U. von Gunten, *Water Research* 39, 3607 (2005)
- [9] K. Kummerer, *Chemosphere* 45, 957 (2001)
- [10] G. Boyd, H. Reemtsma, A. Grimm, S. Mitra, *Canada. Sci. Total Environ.* 311, 135 (2003)
- [11] S. Weigel, U. Berger, E. Jensen, R. Kallenborn, H. Thoresen, H. Huhnerfuss *Chemosphere* 56, 583 (2004)
- [12] T. Scheytt, P. Mersmann, T. Heberer, J. Contam. *Hydrol.* 83, 53 (2006)
- [13] S. Zwiener, F.H. Frimmel, *Water Res.* 34, 1881 (2000)
- [14] F.A. Caliman, M. Gavrilescu, *Clean* 37, 277 (2009)
- [15] T.B. Hayes, P. Case, S. Chiu, *Environmental Health Perspect.* 114, 40 (2006)
- [16] S.K. Khetan, T.J. Collins, *Chem. Rev.* 107, 2319 (2007)
- [17] J.-M. Herrmann, *Catal. Today* 53, 115 (1999)
- [18] S. Malato, J. Blanco, A. Vidal, C. Richter, *Applied Catalysis B: Environmental* 37, 1 (2002)
- [19] U.I. Gaya, A.H. Abdullah, *J. Photochem. Photobiol. C: Photochem. Rev.* 9, 1 (2008)
- [20] C. Reyes, J. Fernandez, J. Freer, M.A. Mondaca, *Catalysis B: Environmental* 37, 1 (2002)
- [21] U.I. Gaya, A.H. Abdullah, *J. Photochem. Photobiol. A: Chemistry* 184, 141 (2006)
- [22] A. Chatzidakis, C. Berberidou, I. Paspaltsis, G. Kyriakou, T. Sklaviadis, I. Poullos, *Water Research* 42, 386 (2008)
- [23] S. Yurdakal, V. Loddo, V. Augugliaro, *Catal. Today* 129, 9 (2007)
- [24] R.A. Palominos, M.A. Mondaca, A. Giraldo, *Catal. Today* 144, 100 (2009)
- [25] J. Mai, W. Sun, L. Xiong, Y. Liu, J. Ni, *Chemosphere*

- [24] 73, 600 (2008)
B.K. Vu, O. Snisarenko, H.S. Lee, E.W. Shin,
[25] *Environ. Techn.* 31(3) 233 (2010)
M. Nelson, W. Hillen, R.A. Greenwald, Tetracycline
[26] in biology, chemistry and medicine (Birkhäuser
Verlag, Switzerland, 2001)
C. Gu, K.G. Karthikeyan, S.D. Sibley, J.A. Pedersen,
[27] *Chemosphere* 66, 1494 (2007)
B.B. Sithole, R.D. Guy, *Water Air Soil Pollution* 32,
[28] 303 (1987)
M. Buckowa, P. Gründler, G.-U. Flechsig,
[29] *Electroanalysis* 17, 440 (2005)
H. Duwensee, M. Adamovski, G.-U. Flechsig, *Int. J.*
[30] *Electrochem. Sci.* 2, 498 (2007)
J. Wang, T. Peng, M.S. Lin, *Bioelectrochemistry*
[31] and *Bioenergetics* 15, 147 (1986)
T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura,
[32] *J. Catal.* 203, 82 (2001)
H.A. Duarte, S. Carvalho, E.B. Paniago,
[33] *A. M. Simas, J. of Pharma. Sciences* 88, 111 (1999)
D.L. Liao, G.S. Wu, B.Q. Liao, *Colloids and Surface*
A: *Physicochem. Eng. Aspects* 348, 270 (2009)
[34]