

Photocatalytic oxidation of dimethoate in aqueous solutions

E. Evgenidou^a, K. Fytianos^{a,*}, I. Poullos^b

^a Environmental Pollution Control Laboratory, Chemistry Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

^b Laboratory of Physical Chemistry, Chemistry Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

Received 14 December 2004; accepted 1 April 2005

Available online 25 May 2005

Abstract

The photocatalytic degradation of dimethoate, an organophosphorous pesticide, has been investigated using TiO₂ and ZnO as catalysts. The degradation kinetics were studied under different conditions such as substrate and photocatalyst concentration, temperature, pH and addition of oxidants. The degradation rates proved to be strongly influenced by these parameters. Comparison between the two catalysts showed that TiO₂ is more efficient to the disappearance of dimethoate and follows first-order kinetics. DOC measurements were carried out in order to evaluate the degree of mineralization. Both catalysts were unable to mineralize dimethoate, but the addition of oxidants improved the efficiency of the processes. Measurements of phosphate, ammonium and sulphate ions gave valuable information about how this process is achieved. Toxicity measurements showed that only the addition of hydrogen peroxide in the illuminated titanium dioxide suspension was able to lead to a complete detoxification of the solution.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Photocatalysis; Dimethoate; TiO₂; ZnO; Oxidant; Mineralization; Toxicity

1. Introduction

Organophosphorous pesticides have been used as an alternative to organochlorine compounds for pest control. Because of the environmental longevity and toxicity of the organochlorines, the agro-industry has increasingly relied upon organophosphate pesticides, which are alleged to be safe due to their rapid environmental degradation [1]. On the other hand, according to many researches, if the organophosphates meet the suitable environmental conditions it is possible to persist in many environmental compartments for long periods of time [2]. Moreover, because of the magnitude of their application they are the chemicals most frequently associated with toxicity to domestic animals and wildlife as well as humans [3]. As a result effective purification methods for removing these pollutants from water are in urgent demand.

Advanced oxidation processes (AOPs) have received increasing attention as an alternative for treating polluted waters. These processes, despite the fact that they make use of

different reacting systems, they are based upon a common property: the production of OH• radicals. These radicals are the second strongest oxidative species after fluorine (reduction potential $E_0 = 2.8$ V) and they attack unselectively most of the organic molecules resulting in a partial or total decomposition [4–7].

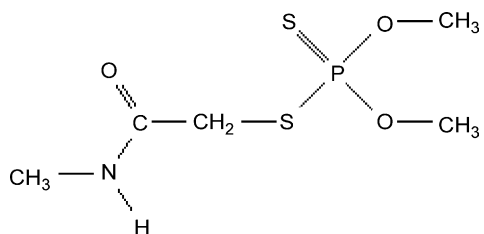
Among these processes, heterogeneous photocatalysis is one of the most promising, since it has already been used successfully for the destruction of a great variety of organic compounds. Furthermore, it gives the opportunity to employ sunlight, so the common drawback of the relatively high cost of UV-lamps and electricity can be overcome. A variety of semiconductor powders (oxides, sulfides, etc.) acting as photocatalysts has been used [6]. Most attention has been given to TiO₂ because of its high photocatalytic activity, its resistance to photocorrosion, its biological immunity and low cost [4,6].

When semiconductors, which are in contact with an electrolytic solution, are illuminated with energy greater than their bandgap energy E_g , excited high-energy states of electron and hole pairs (e^-/h^+) are produced. These species can either recombine in the bulk of the semiconductor and dissipate the input energy as heat or they migrate to surface

* Corresponding author. Tel.: +30 2310997873; fax: +30 2310997873.
E-mail address: fyti@chem.auth.gr (K. Fytianos).

of the semiconductor's particles and react with adsorbed electron donors or electron acceptors. The photogenerated holes act as powerful oxidants and the electrons as powerful reductants and initiate a wide range of chemical redox reactions, which can lead to complete mineralization of organic compounds [8].

In this study, the photocatalytic degradation of dimethoate (*O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate), an organophosphorous insecticide, using TiO_2 and ZnO as catalysts has been investigated. The objectives were: (i) to evaluate the kinetics of pesticide disappearance, (ii) to compare the rates of reaction assisted by the two photocatalysts (iii) to examine the influence of various parameters such as the mass of the catalyst, the initial concentration of dimethoate, the addition of oxidants, change of temperature and pH (iv) to measure the degree of mineralization and (v) to evaluate the detoxification efficiency the studied processes.



Although the photocatalytic degradation of dimethoate, using titanium dioxide, has been studied from previous researchers [9], no significant effort has been made in evaluating the photocatalytic efficiency of ZnO on dimethoate's oxidation and the factors affecting it. Moreover, the already published papers focus on the mineralization of pesticides caused only by titanium dioxide, while scarce information is given concerning the change in the toxicity during treatment. In our study, the mineralization of dimethoate with different reacting systems based on combinations of catalysts with oxidants and their detoxification capacity will be presented.

2. Experimental

Dimethoate analytical grade (99.9% purity) was purchased from Riedel-de-Haen (Germany). HPLC-grade solvents (acetonitrile and water) were supplied by Merck. Hydrogen peroxide (30%) was obtained from Panreac. $\text{K}_2\text{S}_2\text{O}_8$ was purchased from Merck. Titanium dioxide P-25 Degussa (anatase/rutile: 65/35, non-porous, mean size 30 nm, surface area $56 \text{ m}^2 \text{ g}^{-1}$) and ZnO (mean size 110 nm, surface area $9.5 \text{ m}^2 \text{ g}^{-1}$) were used as received. HCl , NaOH and phosphate buffer pH = 7 were used to adjust the pH when necessary. Doubly distilled water was used throughout the work. Stock solutions of dimethoate (1000 mg L^{-1}) were prepared in water, protected from light and stored at 5°C .

Irradiation experiments were carried out in a 500 mL Pyrex UV reactor equipped with a diving Philips HPK 125 W

high-pressure mercury lamp. The lamp was jacked with a water-cooled Pyrex filter restricting the transmission of wavelengths below 290 nm. The tap water cooling circuit maintained the temperature at $30\text{--}35^\circ\text{C}$. Dimethoate solution (10 mg L^{-1} , unless otherwise stated) with the appropriate amount of catalyst was magnetically stirred and equilibrated in the dark for 30 min prior the illumination. The pH was not adjusted unless otherwise stated.

At specific time intervals samples were withdrawn from the reactor. To remove the TiO_2 or ZnO particles the solution samples were filtered through a $0.45 \mu\text{m}$ filter. Dimethoate concentrations were determined by a Shimadzu 10AD liquid chromatograph equipped with a variable wavelength UV detector using a $250 \text{ mm} \times 4.6 \text{ mm}$, C18 nucleosil 100-S column. The mobile phase was a mixture of acetonitrile and water (40/60, v/v) with a flow rate of 1 mL min^{-1} . The detection was realized at 210 nm. Standard solutions of pure compounds were used for quantitative analysis.

In order to evaluate the extend of mineralization total organic carbon (TOC) measurements were carried out by a Shimadzu V-csh TOC analyzer. Nitrate, ammonium, sulfate, and phosphate ions were analyzed spectrophotometrically (with a WTW spectrophotometer) using cuvette tests supplied by WTW following ISO 7890 and 7150 method for nitrate and ammonium respectively and turbidometric and molybdenum blue/ascorbic acid method from standard methods for sulfate and phosphate ions, respectively [10].

For the examination of the toxic properties of the samples collected at specific time intervals throughout the photocatalytic treatment, the luminescent bacteria *V. fischeri* were used. Luminescent bacteria emit light as a by-product of their cellular respiration and metabolic processes. During direct contact with the target compounds, the reduction of the light emission indicates a decreased rate of respiration caused by the presence of toxic compounds. The inhibition of *V. fischeri* was measured by the Microtox test system (Microtox 500 Analyzer, SDI) within short time exposure, 5 and 15 min. The bacteria were in freeze-dried form and were activated prior to use by a reconstitution solution provided by SDI. Since *V. fischeri* is a marine organism an adjustment of the osmotic pressure of the samples was applied, in order to obtain samples with 2% salinity, using a concentrated salt solution (22% NaCl). Toxicity measurements of the samples were conducted using the 82% Microtox screening test protocol (sample concentration 82%) [11]. The pH value of the samples was adjusted to 7 ± 1 , prior to the toxicity tests, by the addition of 0.1N HCl or 0.1N NaOH solutions.

3. Results and discussion

3.1. Preliminary studies

The photocatalytic degradation of dimethoate in the presence or in the absence of the two semiconducting catalysts is presented in Fig. 1. It is clear that the photolysis of a

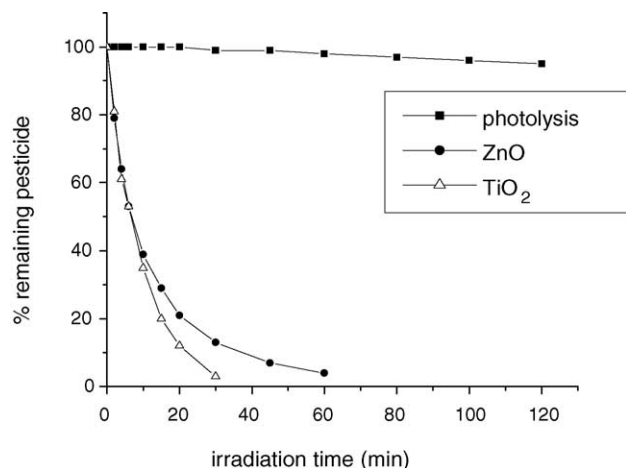


Fig. 1. Photodegradation of dimethoate (10 mg L^{-1}) as function of irradiation time in the presence of TiO_2 (100 mg L^{-1}), ZnO (100 mg L^{-1}) or UV light only, $\text{pH}_0 \sim 7$.

dimethoate solution in the presence of the semiconducting oxides leads to the disappearance of the compound. Under these experimental conditions and in the presence of 100 mg L^{-1} TiO_2 complete disappearance of dimethoate is achieved within 30 min of illumination, while in the presence of the same quantity of ZnO complete disappearance is achieved after 60 min of light exposure. TiO_2 (P-25) appears to be more effective on dimethoate oxidation than ZnO . This result is in agreement with other studies [12,13]. In the absence of a catalyst the photolytic decomposition of the insecticide occurs at a very slow rate and only a 5% reduction of its initial concentration is achieved after 120 min of light exposure. Obviously, the high rate degradation of dimethoate in the presence of TiO_2 and ZnO can clearly be ascribed to the catalysts' activity. Furthermore, the addition of the catalysts without UV radiation had a negligible effect on dimethoate's initial concentration (not shown) indicating the negligible adsorbance of the insecticide on the catalysts' surface.

3.2. Effect of the concentration of the catalyst

In order to study the effect of the catalyst's initial concentration on the photooxidation of dimethoate, experiments were conducted employing different concentrations of TiO_2 and ZnO varying from 10 to 1000 mg L^{-1} (Fig. 2) while using the same initial concentration of dimethoate.

It is obvious that the reaction rate is directly proportional to the mass of catalyst. However, above a certain value the reaction rate levels off and becomes independent of the concentration the catalyst. This limit depends on the geometry and the working conditions of the reactor and corresponds to the optimum of light absorption. Above this concentration, the suspended particles of the catalysts block the UV-light passage and increase the light scattering [7,14–18]. The optimum catalyst loading was found from previous studies to be dependent on the initial solute concentration [19]. In this

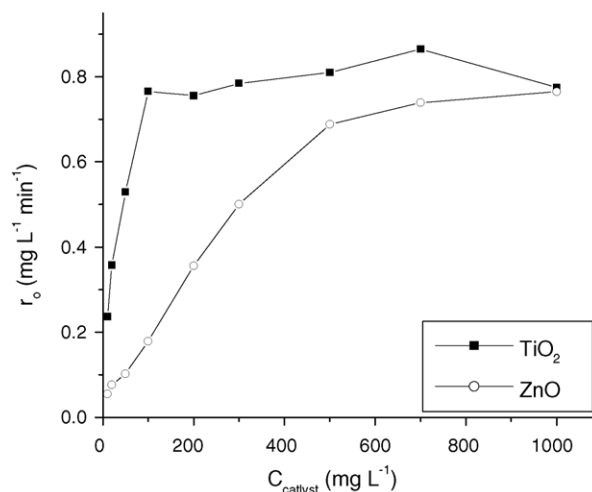


Fig. 2. Dependence of the initial reaction rate r_0 on the concentration of the catalyst ($[\text{dimethoate}] = 10 \text{ mg L}^{-1}$). TiO_2 , $\text{pH}_0 = 6.5$; ZnO , $\text{pH}_0 = 7.4$.

study, it can be observed from Fig. 2, that the optimum value for TiO_2 is 100 mg L^{-1} and for ZnO 500 mg L^{-1} . This difference is ascribed to the catalysts characteristics—a combination of the surface area and the particle size. TiO_2 exhibits larger surface area and a smaller particle size which are responsible from one hand, for higher reaction rates at small concentrations, and from the other, for provoking more easily light scattering while on the contrary, ZnO requires higher amounts in order to achieve similar reaction rates before light scattering takes place [19].

Furthermore, the decrease of the reaction rates at high catalyst concentration are due to other phenomena that may take place like agglomeration (particle–particle interactions) which result in a loss of surface area available for light-harvesting [19].

Due to the great difference in the surface area of both catalysts, the comparison between them was not always possible and consequently the optimum amount of each catalyst was selected, according to Fig. 2, to work with throughout the study (100 mg L^{-1} for TiO_2 and 500 mg L^{-1} for ZnO).

3.3. Effect of the concentration of dimethoate

According to previous studies, the influence of the initial concentration of the solute on the photocatalytic degradation rate of the most organic compounds is described by pseudo-first-order kinetics which is rationalized in terms of the Langmuir–Hinshelwood model, modified to accommodate reactions occurring at a solid–liquid interface [20–23]. On the assumption of no competition with reaction byproducts, the simplest representation for the rates of disappearance of dimethoate is given by

$$r_0 = -dC/dt = k_r K C_0 / (1 + K C_0) \quad (1)$$

where r_0 is the initial rate of disappearance of dimethoate and C_0 its initial concentration. K represents the equilibrium

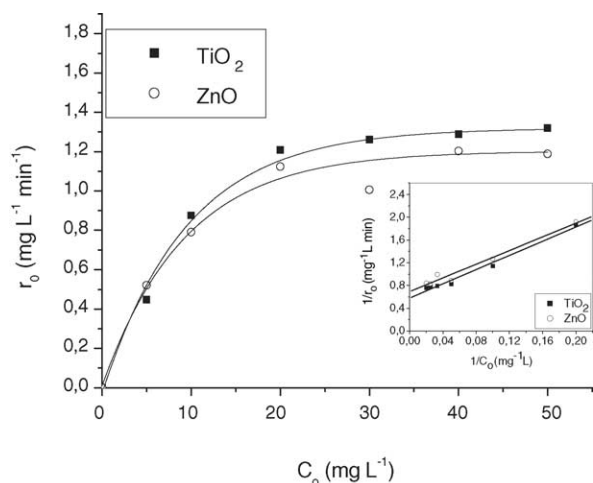


Fig. 3. Dependence of the initial reaction rate r_0 , on the initial concentration of dimethoate C_0 ($\text{TiO}_2 = 100 \text{ mg L}^{-1}$ $\text{pH}_0 = 6.5$, $\text{ZnO} = 500 \text{ mg L}^{-1}$ $\text{pH}_0 = 7.2$). Inset: linear transform of $1/r_0$ vs. $1/C_0$ according to Eq. (2).

adsorption constant of dimethoate and k_r reflects the limiting reaction rate at maximum coverage for the experimental conditions. A standard means of using this equation is to demonstrate linearity of data when plotted as the inverse initial rate versus inverse initial concentration

$$1/r_0 = 1/k_r + 1/k_r K \times 1/C_0 \quad (2)$$

Photocatalytic experiments in the presence of TiO_2 and ZnO were carried out using various initial concentrations of dimethoate ($5\text{--}50 \text{ mg L}^{-1}$). The dependence of dimethoate's concentration on irradiation time was plotted and the initial reaction rate, r_0 values were independently obtained from these curves, by the linear fit using only the experimental data obtained during the first minutes of illumination until 20% reduction was achieved, in order to minimize variations as a result of competitive effects of intermediates, pH changes, etc [20].

The dependence of the initial reaction rate r_0 on the initial concentration of dimethoate is depicted in Fig. 3. It is obvious that the rate increases with the increase of the initial concentration of dimethoate until it reaches a saturation value at high concentrations of the insecticide. Above 20 mg L^{-1} , the initial reaction rate starts to become constant, for both catalysts.

As indicated in the inset of Fig. 3, the plot of the reciprocal initial rate r_0^{-1} as a function of the reciprocal initial concentration C_0^{-1} yields a straight line. The linear transform of this expression yields $k_r = 1.7 \text{ mg L}^{-1} \text{ min}^{-1}$ ($7.5 \times 10^{-6} \text{ M min}^{-1}$) and $K = 0.09 \text{ mg}^{-1} \text{ L}$ ($2.4 \times 10^4 \text{ M}^{-1}$) for the TiO_2 and $k_r = 1.4 \text{ mg L}^{-1} \text{ min}^{-1}$ ($6.3 \times 10^{-6} \text{ M min}^{-1}$) and $K = 0.04 \text{ mg}^{-1} \text{ L}$ ($2.7 \times 10^4 \text{ M}^{-1}$) for the ZnO . These constants reflect to the experimental conditions that has been used and they have no absolute meaning. Comparison between the k_r of TiO_2 and the k_r of ZnO cannot be achieved as the catalysts' characteristics are completely different.

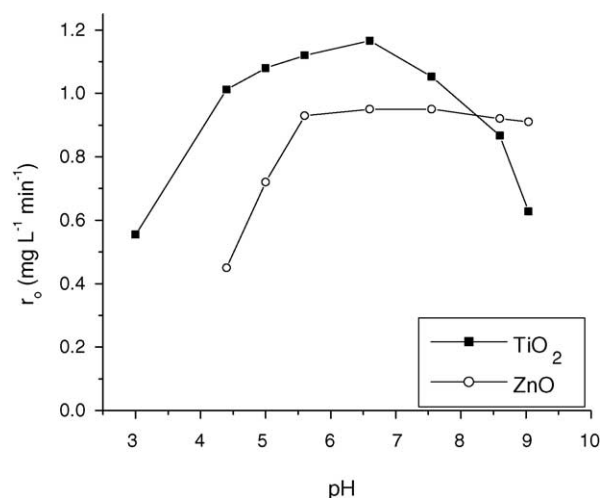


Fig. 4. Effect of pH on the initial photodegradation rate of dimethoate (10 mg L^{-1}) in the presence of TiO_2 (100 mg L^{-1}), and ZnO (500 mg L^{-1}).

The rate constants (k_r) are useful for comparisons between reactants and can only be made when using the same catalyst and the same illumination source [24].

3.4. Effect of pH

According to previous studies, pH appears to play an important role in the photocatalytic process of various pollutants [15,16,18–20,25–28]. The influence of the initial pH value on the initial photodegradation rate of dimethoate for the TiO_2 and ZnO suspensions is demonstrated in Fig. 4.

In the illuminated TiO_2 system, the effect of pH on the photocatalytic reaction is generally attributed to the surface charge of TiO_2 . The point of zero charge (pzc) of TiO_2 is 6.3 and at pH values lower than 6.3 the catalyst's surface is positively charged and at higher pH values it is negatively charged. Electrostatic attraction or repulsion between the catalyst's surface and the organic molecule is taking place, depending on the ionic form of the organic compound (anionic or cationic) and consequently enhances or inhibits, respectively, the photodegradation rate. In Fig. 4 it is observed that the higher degradation rate occurs at $\text{pH} = 6.5$ which is near the point of zero charge of the catalyst. Because of the positive charge of amino group and the negative charge of the carbonyl group complicated interactions between the molecules and the catalyst are taking place at acidic or alkaline pH. When the catalyst has no charge the molecules probably, are allowed to reach easily the catalyst's surface and achieve higher reaction rates [25].

In the ZnO system an increase is observed as pH is increased from 4.5 to 5.4 (approximately two-fold increase). At pH values higher than 5.4, an almost steady initial reaction rate is observed with a negligible decrease as we reach high pH values ($\text{pH} = 9$). The low initial reaction rates at acidic pH are attributed to dissolution and photodissolution of ZnO (see Fig. 13) [29].

3.5. Effect of the addition of an oxidant

The addition of an oxidant into a semiconductor suspension has been proven to enhance the photodegradation rate of a variety of organic pollutants [12,18,20,30–36]. In our study the addition of both hydrogen peroxide (H_2O_2) and peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$) was evaluated.

In order to examine the role of hydrogen peroxide, experiments of the photocatalytic degradation of dimethoate employing different initial concentrations of the oxidant were conducted. In Fig. 5 the initial rates of reaction versus the concentration of the oxidant are presented. It is obvious that until the concentration of 6 mM hydrogen peroxide increases the photodegradation rate by approximately a factor of 2. This is because hydrogen peroxide can act as an electron acceptor and consequently it can promote the charge separation. Moreover it can also produce OH^\bullet radicals according to the following equations:



Increasing further the concentration of peroxide, no significant change in the reaction rate is observed. On the contrary a slight decrease is taking place because at high concentrations, hydrogen peroxide may act as a hole or OH^\bullet scavenger. Therefore an optimal concentration must be designated in order to achieve the best results. According to previous authors this concentration depends on the H_2O_2 /contaminant molar ratio [35].

On the other hand an opposite effect is observed in the case of zinc oxide (Fig. 6). The addition of the oxidant causes a decrease of the photooxidation rate of dimethoate. This is probably due to its low adsorption on the zinc oxide's surface. When TiO_2 and ZnO are illuminated hydrogen peroxide is produced. In the case of titanium dioxide small concentrations of hydrogen peroxide have been detected because

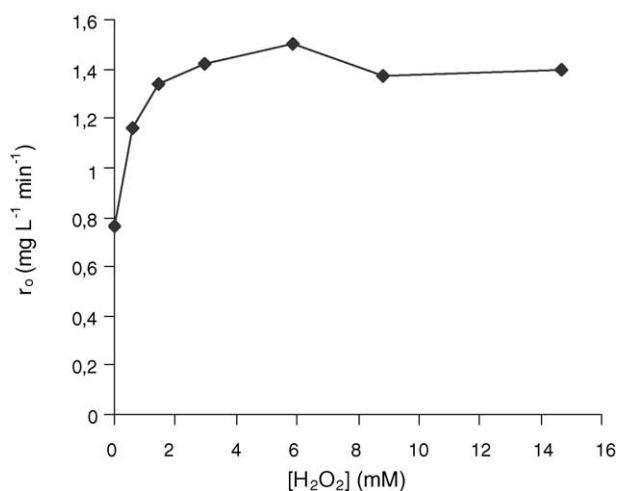


Fig. 5. Effect of the H_2O_2 on the photocatalytic degradation rate of dimethoate (10 mg L^{-1}) in the presence of TiO_2 (100 mg L^{-1}).

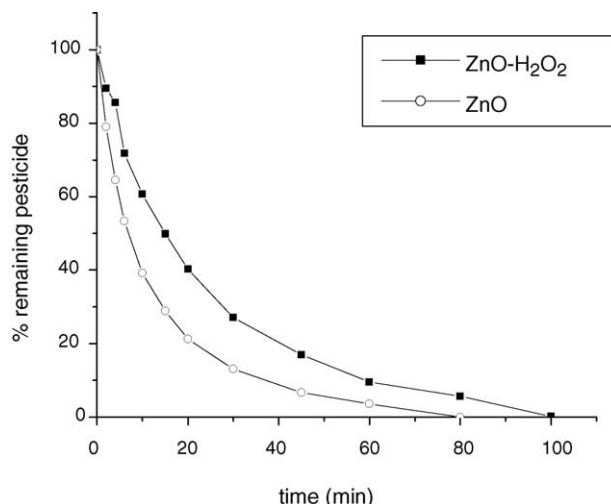


Fig. 6. Effect of the addition of hydrogen peroxide (100 mg L^{-1}) on the photocatalytic degradation of dimethoate (10 mg L^{-1}) in the presence of ZnO (500 mg L^{-1}).

the latter can be easily adsorbed on TiO_2 surface and consequently is degraded more efficiently. On the other hand, an increasing concentration of peroxide has been measured during illumination of ZnO suspensions due to its low adsorption on ZnO surface [37–39]. In this case, addition of peroxide will have no effect or moreover, it may cause a negative effect because, as previously noted, an excess of peroxide can act as a radical or a hole scavenger. For this reason the system ZnO– H_2O_2 was not further investigated.

The effect of adding another electron scavenger (peroxydisulfate) that has been used with promising results [34,35] is presented in Fig. 7. Addition of $\text{K}_2\text{S}_2\text{O}_8$ in the photocatalytic system causes an increase of the reaction rate for both TiO_2 and ZnO suspensions. The reactions where $\text{K}_2\text{S}_2\text{O}_8$ is involved and responsible of its efficiency are the following:

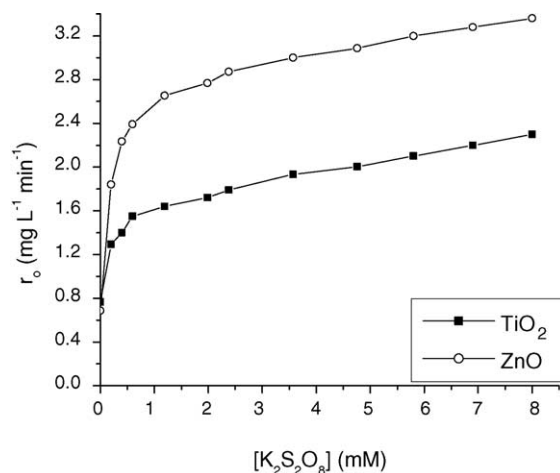
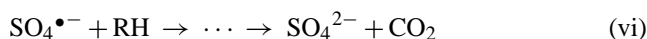
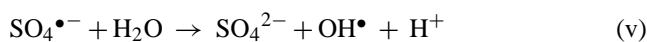


Fig. 7. Effect of the $\text{K}_2\text{S}_2\text{O}_8$ on the photocatalytic degradation rate of dimethoate (10 mg L^{-1}) in the presence of TiO_2 (100 mg L^{-1} , $\text{pH}_0 = 6.2$) and ZnO (500 mg L^{-1} , $\text{pH}_0 = 7.4$).

Table 1

Dimethoate initial degradation rates (r_0) and percentage of degradation (after 10 min of illumination) under various experimental conditions

Catalyst or oxidant added	r_0 (mg L ⁻¹ min ⁻¹)	Percentage of degradation (after 10 min of irradiation)
TiO ₂ (100 mg L ⁻¹)	0.77 ± 0.04	65
ZnO (500 mg L ⁻¹)	0.69 ± 0.07	61
H ₂ O ₂ (1 mM)	0.09 ± 0.01	10
K ₂ S ₂ O ₈ (1 mM)	0.52 ± 0.03	44
TiO ₂ + H ₂ O ₂ (100 mg L ⁻¹ + 1 mM)	1.34 ± 0.22	77
TiO ₂ + K ₂ S ₂ O ₈ (100 mg L ⁻¹ + 1 mM)	1.55 ± 0.26	87
ZnO + H ₂ O ₂ (500 mg L ⁻¹ + 1 mM)	0.39 ± 0.06	39
ZnO + K ₂ S ₂ O ₈ (500 mg L ⁻¹ + 1 mM)	2.39 ± 0.66	99



K₂S₂O₈ traps the photogenerated electron, preventing the recombination with the positive hole and at the same time produces the sulfate radical, which is a very strong oxidizing agent (reduction potential of SO₄^{•-} $E_0 = 2.6$ V).

Using small concentrations of peroxydisulfate (until 1 mM), a sharp increase of the initial reaction rate is observed for both catalysts. A further increase of the concentration of the added oxidant, still gives a rise to the initial photodegradation rate even at very high concentrations. Unlike hydrogen peroxide, high concentrations of peroxydisulfate are not detrimental to the reaction rate and no dependence is observed on the oxidant/contaminant molar ratio [35].

Comparing the two oxidants, peroxydisulfate appears to be more effective than hydrogen peroxide since it is able to achieve higher reaction rates, it does not act as a scavenger at high concentrations while there is no dependence on the oxidant/contaminant molar ratio and it is effective on both photocatalytic systems.

However, the ability of H₂O₂ and K₂S₂O₈ to enhance the photodegradation of dimethoate is not only due to the entrapment of the photogenerated electrons but, also due to their own ability to absorb light and act as sensitizers through the production of hydroxyl and sulfate radicals. Experiments with UV light and the oxidants, without the catalyst, were performed and showed that both oxidants are able to cause photooxidation of the insecticide. In Table 1 the initial reaction rates and the percentage of dimethoate degradation after 10 min of treatment are presented. Consequently, the improvement of the photocatalytic degradation of dimethoate by the addition of oxidants is not only due to prevention of the recombination of the e⁻/h⁺ pair but also due to the photolytic activity of the oxidant. Blank experiments with the oxidants without the catalyst or UV light showed a negligible degradation of the insecticide.

3.6. Effect of temperature

In order to evaluate the effect of temperature on the degradation rate of dimethoate experiments at different tempera-

tures, varying from 15 to 65 °C, were carried out for both illuminated TiO₂ and ZnO suspensions. Fig. 8 shows the Arrhenius plot of ln k versus T^{-1} from which the activated energy of dimethoate degradation was calculated. The E_a for TiO₂ system is 22.9 kJ mol⁻¹ and for the ZnO system 21.5 kJ mol⁻¹. It is obvious that the increase of the temperature causes an increase to the reaction rate. The enhancement of the photooxidation is probably due to the increasing collision frequency of molecules. Irradiation is believed to be the primary source of e⁻/h⁺ pairs at ambient temperature because the band gap is too high to overcome by thermal excitation [40].

3.7. Mineralization studies

A complete degradation of an organic molecule by photocatalysis normally leads to the conversion of all its carbon atoms to gaseous CO₂, and the heteroatoms into inorganic anions that remain in the solution. In order to study the total mineralization of dimethoate, two sets of determinations were carried out: (a) dissolved organic carbon (DOC) and (b) inorganic ions formation, as a function of irradiation time.

In Fig. 9a and b DOC reduction and formation of ammonium, sulfate and phosphate ions release is presented for both TiO₂ and ZnO systems. In the illuminated TiO₂ suspension

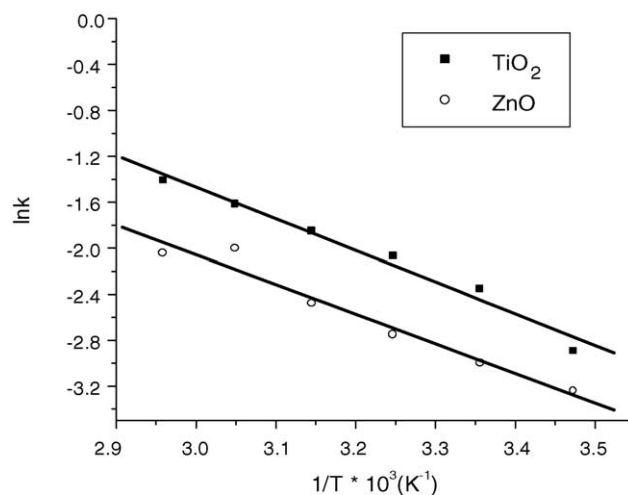


Fig. 8. Effect of temperature on photocatalytic degradation of dimethoate (10 mg L⁻¹) in the presence of (a) 100 mg L⁻¹ TiO₂ and (b) 500 mg L⁻¹ ZnO.

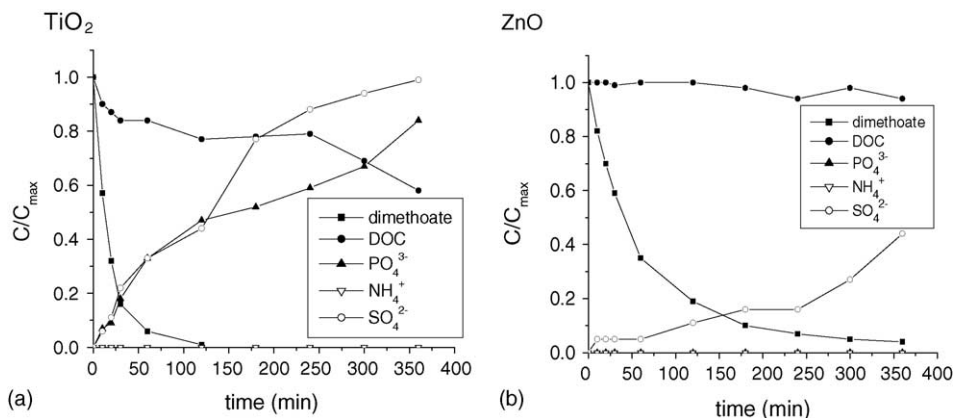


Fig. 9. Dimethoate/DOC reduction and $SO_4^{2-}/PO_4^{3-}/NH_4^+$ release as a function of irradiation time, dimethoate = 25 mg L^{-1} : (a) $TiO_2 = 100 \text{ mg L}^{-1}$, $\text{pH} = 6.5$ and (b) $ZnO = 500 \text{ mg L}^{-1}$, $\text{pH} = 7.4$.

complete disappearance of the insecticide occurs after 2 h of irradiation while DOC, by this time is only 20% reduced indicating the formation of intermediates. After 6 h of treatment DOC reaches a 40% reduction which implies that titanium dioxide is not able to degrade the arisen by-products thus requiring longer irradiation times or higher quantities. Release of sulfate and phosphate ions proceeds rather simultaneously in the first 2 h but then sulfates maintain the high rate and reach their maximum after 6 h while phosphate ions release proceeds slower and finally they reach the 90% of the expected amount. No ammonium ions are observed implying the formation of nitrogen containing intermediates.

In the ZnO system the overall process follows a slower rate (Fig. 9b). Complete disappearance of dimethoate is achieved after 5 h of illumination while a negligible reduction of DOC is observed (only 5% after 6 h). Moreover, only sulfate ions are released which they reach the 50% of the expected amount. According to previous studies attack of the P=S bond by OH^\cdot radicals occurs firstly, in the case of phosphorothioates leading to formation of oxon derivatives [41] which, in our case, appear to be persistent under the illumination of ZnO suspensions. Moreover it is likely to have a release of phosphate ions but not be able to measure as they may be trapped by ions of zinc (from dissolution of ZnO) to form $Zn_3(PO_4)_2$ which is insoluble in water.

In Fig. 10, mineralization under the $TiO_2\text{-}H_2O_2$ system is depicted. Comparing to the TiO_2 system we obtain better results since higher degradation rates and mineralization percentage are achieved. Complete disappearance of dimethoate is observed in the first 60 min and DOC is 90% reduced after 6 h of illumination. Release of sulfate and phosphate ions is also faster, in the first hours of irradiation, reaching the maximum of the expected amount after 6 and 4 h, respectively. In this system, ammonium ions release is also observed, reaching almost the 50% of expected amount. According to previous studies nitrogen containing compounds give rise to both ammonium and nitrate atoms. The NH_4^+/NO_3^- ratio depends on the irradiation time, the pH of the solution and the oxida-

tion state of nitrogen [42]. In our case no nitrate ions release was observed.

In Fig. 11 the effect of peroxydisulfate on the mineralization of dimethoate under illuminated TiO_2 and ZnO suspensions, is presented. Sulfate ions release was not possible to be measured since high concentrations of sulfate ions are already present in the solution because of peroxydisulfate ions. It is obvious that the addition of peroxydisulfate enhances the mineralization of dimethoate and in the case of TiO_2 , complete disappearance is achieved in less than 60 min and DOC is 98% reduced after 4 h of illumination. Both phosphate and ammonium ions reach the expected amount in the first 2 h (100% and 120%, respectively).

In the ZnO system the effect of peroxydisulfate is even more impressive since complete disappearance of the insecticide is observed in 45 min. DOC is 95% reduced by the first 3 h of treatment. Both phosphate and ammonium ions reach the expected amount in less than 2 h. Since $Zn_3(PO_4)_2$

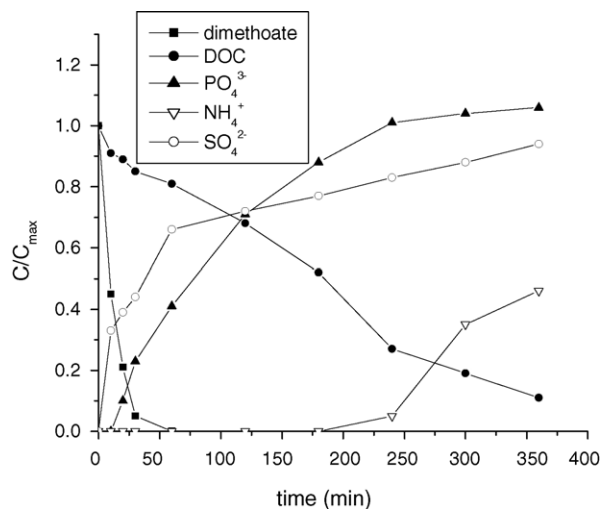


Fig. 10. Dimethoate/DOC reduction and $SO_4^{2-}/PO_4^{3-}/NH_4^+$ release as a function of irradiation time in the presence of $TiO_2 = 100 \text{ mg L}^{-1}$ and $H_2O_2 = 3.1 \text{ mg L}^{-1}$ ($\text{pH}_0 = 6$, dimethoate = 25 mg L^{-1}).

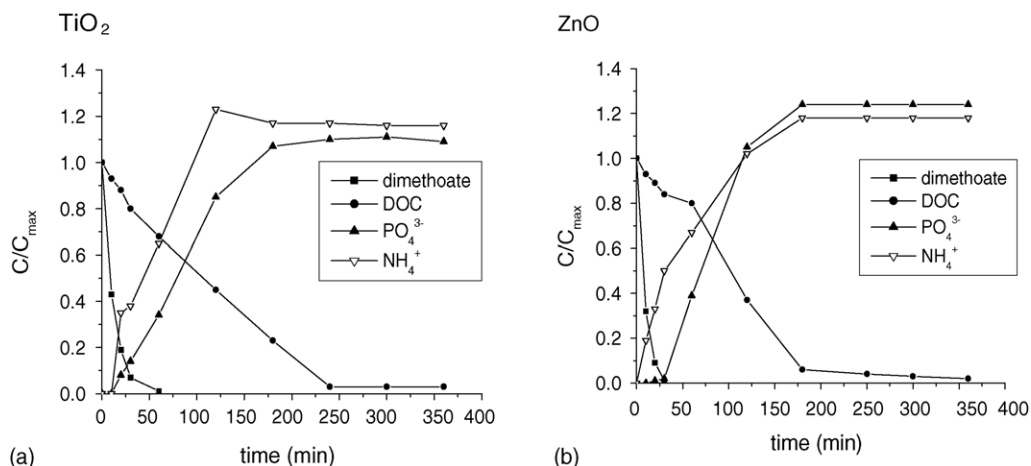


Fig. 11. Dimethoate/DOC reduction and $\text{PO}_4^{3-}/\text{NH}_4^+$ ions release as a function of irradiation time in the presence of (a) $\text{TiO}_2 = 100 \text{ mg L}^{-1}$, $\text{K}_2\text{S}_2\text{O}_8 = 3.1 \text{ mM}$ and (b) $\text{ZnO} = 100 \text{ mg L}^{-1}$, $\text{K}_2\text{S}_2\text{O}_8 = 3.1 \text{ mM}$ ($\text{pH}_0 = 6$, dimethoate = 25 mg L^{-1}).

is soluble in acids, it cannot be formed under illuminated peroxydisulfate because of the production of H_2SO_4 . Peroxydisulfate appears to promote degradation of dimethoate for both systems (TiO_2 and ZnO) and almost complete mineralization is achieved in short time.

3.8. Toxicity measurements

The photocatalytic treatment of dimethoate solutions with titanium dioxide or zinc oxide in combination with oxidants appeared to be quite effective on the degradation and mineralization of the insecticide. However, when complete mineralization is not achieved it is possible that the final products could be more toxic than the parent compounds. For this reason, toxicity measurements during and at the end of treatment are indispensable. In our study, toxicity measurements of the treated solutions were carried out in order to give a more complete evaluation of the efficiency of the technologies that have been used. The toxicity of the samples collected from different stages of the treatment was measured using the Microtox test. The results obtained after 15 min exposure of the bacteria to the samples are presented to Fig. 12.

It is obvious that variation in toxicity during treatment is depended on the method that it is used. For the TiO_2 system the toxicity appears a slight increase in the first 2 h of irradiation but finally drops from 69% to 59%. According to Fig. 9, 2 h are required in order to achieve complete disappearance of dimethoate. Consequently the compounds that are produced firstly, during dimethoate oxidation (probably the oxon derivatives), are more toxic than the parent compound. After the first 2 h, as mineralization proceeds, toxicity is also reducing.

For the $\text{TiO}_2\text{-H}_2\text{O}_2$ system, since more intense oxidative conditions are present in the illuminated solution, we observe a slight reduction in the toxicity until the first 60 min of treatment, which is the time required for complete disappearance of dimethoate (Fig. 10), while afterwards a sharp decrease is

observed, achieving complete detoxification of the solution in 3 h. On the contrary, in the $\text{TiO}_2\text{-K}_2\text{S}_2\text{O}_8$ system, toxicity is not directly depended on mineralization. Although almost complete mineralization is achieved in 4 h, toxicity is only slightly reduced from 69% to 58%. This slight reduction of toxicity cannot be attributed to the presence of unconsumed peroxydisulfate since toxicity measurements of a blank solution of peroxydisulfate with concentration of 3.1 mM (as high as the initial concentration of $\text{K}_2\text{S}_2\text{O}_8$) showed no inhibition effect. Moreover, blank experiments showed that sulfate ions which are produced from the consumption of $\text{K}_2\text{S}_2\text{O}_8$ during the photocatalytic oxidation exhibit also a non toxic effect. Consequently, it can be attributed to the action of peroxydisulfate, causing probably, a change of the oxidation mechanism. Different by-products may be produced and synergistic effects may take place that prevent the large decrease of the toxicity of the treated solution.

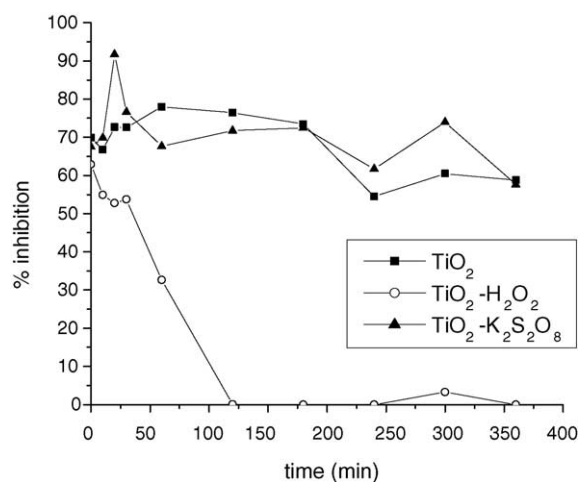


Fig. 12. Toxicity evolution as a function of irradiation time in the presence of $\text{TiO}_2 = 100 \text{ mg L}^{-1}$, $\text{TiO}_2 = 100 \text{ mg L}^{-1} + \text{H}_2\text{O}_2 = 3.12 \text{ mM}$, $\text{TiO}_2 = 100 \text{ mg L}^{-1} + \text{K}_2\text{S}_2\text{O}_8 = 3.1 \text{ mM}$.

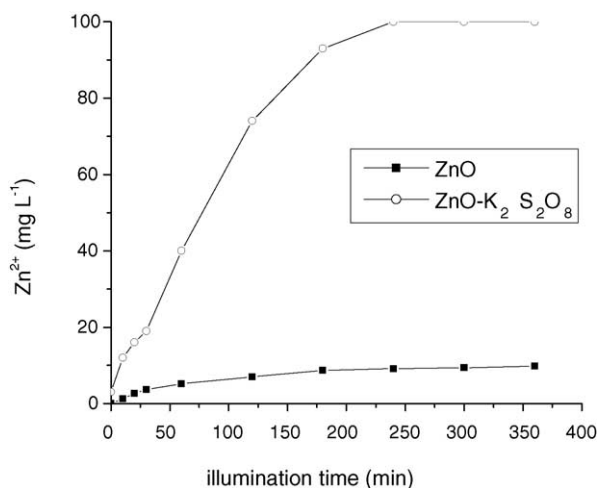


Fig. 13. Concentration of zinc in the solution as a function of irradiation time in the presence of (a) ZnO = 500 mg L⁻¹ and (b) ZnO = 100 mg L⁻¹ and K₂S₂O₈ = 3.1 mM.

Toxicity during treatment with ZnO and ZnO/K₂S₂O₈ was also measured and found to be increased by the first hour of illumination. This increase was provoked by the dissolution and photodissolution of ZnO during the degradation process [43] and it was confirmed by measurements of Zn²⁺ presented in Fig. 13 (EC₅₀ of zinc is 1.62 mg L⁻¹ [44]) and by the difference in the toxic response between the 5 and 15 min exposure, which is characteristic of the metal ions [45]. Dissolution of zinc is more obvious with the addition of peroxydisulfate due to the production of sulfuric acid and significant drop of pH during photocatalysis. Unfortunately, any conclusion concerning the toxicity of the photoproducts was impossible since zinc was not removed from the solution and such treatment was out of the scope of the study. For this reason, toxicity measurements under ZnO suspensions are not presented in this study.

4. Conclusions

The photocatalytic oxidation of dimethoate has been studied using TiO₂ and ZnO as catalysts. Titanium dioxide proved to be more efficient photocatalyst since the oxidation and decomposition of the insecticide proceeded at higher reaction rates. Complete mineralization was not achieved in both systems and probably needs longer irradiation time or higher quantities of the catalysts. The photooxidation of dimethoate followed first-order kinetics and parameters such as temperature and concentration of the catalyst play an important role affecting the reaction rate. With the addition of oxidants into illuminated TiO₂ suspensions a synergistic effect was observed that leads to an enhancement and improvement of the efficiency of the process, achieving mineralization of the organic compound.

In the TiO₂ system the toxicity was only slightly reduced after 6 h of treatment. Moreover, only the addition of perox-

ide was able to achieve complete detoxification of the treated solution since the addition of peroxydisulfate changes the oxidation mechanism and leads to a small decrease of the toxicity. The dissolution of zinc, in the systems with zinc oxide, did not permit to draw conclusions about the toxicity of the intermediate and final products and also raise questions regarding its use as a photocatalyst. Although degradation and mineralization of dimethoate was achieved, ZnO cannot be considered as a good catalyst since dissolution and photodissolution of zinc takes place in such extent and ZnO concentration does not stay intact at the end of the treatment increasing the toxicity of the solution.

Acknowledgement

This study was financed by EPEAEK under the framework of the scholarships program "HRAKLEITOS".

References

- [1] H. Floesser-Mueller, W. Schwack, *Rev. Environ. Contam. Toxicol.* 172 (2001) 129–228.
- [2] K.V. Ragnarsdottir, *J. Geol. Soc.* 157 (2000) 859–876.
- [3] M.A. Gallo, N.J. Lawryk, in: W.J. Hayes Jr., E.R. Laws Jr. (Eds.), *Handbook of Pesticide Toxicology*, Academic Press, 1988, p. 917.
- [4] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, *Catal. Today* 53 (1999) 51–59.
- [5] S. Chiron, A. Fernandez-Alba, A. Rodriguez, E. Garcia-Calvo, *Water Res.* 34 (2000) 366–377.
- [6] D.S. Bhatkhande, V.G. Pangarkar, A. Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2001) 102–116.
- [7] J.-M. Herrmann, *Catal. Today* 53 (1999) 115–129.
- [8] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69–96.
- [9] C. Domínguez, J. García, M.A. Pedraz, A. Torres, M.A. Galán, *Catal. Today* 40 (1998) 85–101.
- [10] APHA, AWWA, WPCF, *Standard Methods for the Examination of Water and Waste Water*, 16th ed., APHA, AWWA, WPCF, 1985.
- [11] Microbics Corporation, *Microtox Manual, A Toxicity Testing Handbook*, vols. 1–5, Microbics Corporation, Carlsbad, CA, USA, 1992.
- [12] E. Evgenidou, K. Fytianos, I. Poulios, in: T.D. Lekkas (Ed.), *Proceedings of the Eighth International Conference on Environmental Science and Technology*, Lemnos Island, Greece, 2003.
- [13] S.A. Naman, Z.A.-A. Khammas, F.M. Hussein, *J. Photochem. Photobiol. A: Chem.* 153 (2002) 229.
- [14] J.-M. Herrmann, G. Guillard, J. Disdier, C. Lehaut, S. Malato, *J. Blanco, Appl. Catal. B: Environ.* 35 (2002) 281–294.
- [15] A.B. Prevot, M. Vincenti, A. Bianciotto, E. Pramauro, *Appl. Catal. B: Environ.* 22 (1999) 149–158.
- [16] D. Robert, B. Dongui, J.-V. Weber, *J. Photochem. Photobiol. A: Chem.* 156 (2003) 195–200.
- [17] J.P. Percherancier, R. Chapelon, B. Pouyet, *J. Photochem. Photobiol. A: Chem.* 87 (1995) 261–266.
- [18] N. Daneshvar, D. Salari, A.R. Khataee, *J. Photochem. Photobiol. A: Chem.* 6239 (2003) 1–6.
- [19] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, *Sol. Energy Mater. Sol. Cells* 77 (2003) 65–82.
- [20] I. Poulios, A. Avranas, E. Rekliti, A. Zouboulis, *J. Chem. Technol. Biotechnol.* 75 (2000) 205–212.

- [21] I.K. Konstantinou, T.M. Sakellarides, V.A. Sakkas, T.A. Albanis, *Appl. Catal. B: Environ.* 42 (2003) 319–335.
- [22] C.S. Turci, D.F. Ollis, *J. Catal.* 122 (1990) 178–192.
- [23] J. Cunningham, G. Al-Sayyid, S. Srijaranai, Adsorption of model pollutants onto TiO₂ particles in relation to photoremediation of contaminated water, in: G. Helz, R. Zepp, D. Crosby (Eds.), *Aquatic and Surface Photochemistry*, Lewis Publishers/CRC Press, 1994, pp. 317–348.
- [24] D.F. Ollis, E. Pelizzetti, N. Seprone, Heterogenous photocatalysis in the environment: application to water purification, in: N. Seprone, E. Pelizzetti (Eds.), *Photocatalysis, Fundamentals and Applications*, John Wiley & Sons Publishers, USA, 1989, pp. 604–637.
- [25] D.S. Bhatkhande, V.G. Pangarkar, A.A.M.C. Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2001) 102–116.
- [26] A. Piscopo, D. Robert, J.V. Weber, *Appl. Catal. B: Environ.* 35 (2001) 117–124.
- [27] C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, *Catal. Today* 76 (2002) 235–246.
- [28] C.A.K. Gouvea, F. Wypych, S.G. Moraes, N. Durán, N. Negata, P. Peralta-Zamora, *Chemosphere* 40 (2000) 433–440.
- [29] P. Spathis, I. Poullos, *Corros. Sci.* 37 (1995) 673–680.
- [30] I. Poullos, M. Kositzi, A. Kouras, *J. Photochem. Photobiol. A: Chem.* 115 (1998) 175–183.
- [31] S. Malato, J. Blanco, A. Vidal, C. Richter, *Appl. Catal. B: Environ.* 967 (2001) 1–15.
- [32] R.-A. Doong, W.-H. Chang, *J. Photochem. Photobiol. A: Chem.* 116 (1998) 221–228.
- [33] K. Harada, T. Hisanga, K. Tanaka, *Water Res.* 24 (1990) 1415–1417.
- [34] S. Malato, J. Blanco, C. Richter, P. Fernández, M.I. Maldonado, *Sol. Energy Mater. Sol. Cells* 64 (2000) 1–14.
- [35] S. Malato, J. Blanco, M.I. Maldonado, P. Fernández-Ibáñez, A. Campos, *Appl. Catal. B: Environ.* 28 (2000) 163–174.
- [36] R.-A. Doong, W.-H. Chang, *J. Photochem. Photobiol. A: Chem.* 107 (1997) 239–244.
- [37] J.R. Harbour, J. Tromp, M.L. Hair, *Can. J. Chem.* 63 (1985) 204–208.
- [38] A.H. Boonstra, C.A.H.A. Mutsaers, *J. Phys. Chem.* 79 (1975) 1940–1943.
- [39] C. Korman, D.W. Bahnemann, M.R. Hoffmann, *Environ. Sci. Technol.* 22 (1988) 789–806.
- [40] M.-C. Lu, G.-D. Roam, J.-N. Chen, C.-P. Huang, *J. Photochem. Photobiol. A: Chem.* 76 (1993) 103–110.
- [41] I. Konstantinou, T. Albanis, *Appl. Catal. B: Environ.* 42 (2003) 319–335.
- [42] G. Low, S. McEvoy, R. Matthews, *Environ. Sci. Technol.* 25 (1991) 460–467.
- [43] E. Evgenidou, K. Fytianos, I. Poullos, *Appl. Catal. B: Environ.* 59 (2005) 83–91.
- [44] N.H. Ince, N. Dirilgen, I.G. Apikyan, G. Tezcanli, B. Üstün, *Arch. Environ. Contam. Toxicol.* 36 (1999) 365–372.
- [45] K. Kaiser, Palabrica, *Water Pol. Res. J. Can.* 26 (1991) 361–431.