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Photodegradation of metamitron (4-amino-6-phenyl-3-methyl-1,2,4-triazin-5(4H)-one) on TiO_2

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Abstract

Photodegradation of metamitron in aqueous solution (i) on a plate photoreactor with immobilized TiO_2 layer and (ii) in a tube photoreactor in the presence of quantum sized Q-TiO_2 particles was investigated and compared. Both processes, heterogeneous photocatalysis and homogeneous direct photolysis, took part on the overall photodegradation of metamitron. Deaminometamitron (6-phenyl-3-methyl-1,2,4-triazin-5(4H)-one), hydroxymetamitron (4-amino-6-(2′-hydroxyphenyl)-3-methyl-1,2,4-triazin-5(4H)-one) and deaminohydroxymetamitron (6-(2′-hydroxyphenyl)-3-methyl-1,2,4-triazin-5(4H)-one) were identified as main products. A reaction scheme of these phototransformations was proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TiO_2; Metamitron; Photodegradation

1. Introduction

Chemical substances derived from a structure of 4-amino-1,2,4-triazin-5(4H)-one exhibit herbicidal activity. Substances of this class, such as metribuzin and metamitron, are used worldwide. These compounds are chemically stable and can penetrate slowly through the soil and cause a long-term contamination of underground resources of drinking water.

Properties of these substances have been recently studied by means of electrochemistry [1–4]. Their reduction led to dihydroderivatives that consecutively underwent acid catalyzed hydrolysis accompanied with opening of the trazine ring [5]. Authors supposed that these reactions could take place in the soil as one of possible destruction pathways of the triazine ring.

Photodegradation of metamitron has been studied by several authors [6–9]. Palm et al. [6] found that the direct photolysis of metamitron in aerated aqueous solutions yielded to 6-phenyl-3-methyl-1,2,4-triazine-5(4H)-one (deaminometamitron) as a main product. The phototransformation was fast and followed the first-order kinetics. Applying typical sunlight intensities, the estimated lifetimes (rate constants) of metamitron were between 0.4 h (June, $k = 5 \times 10^{-4}\,s^{-1}$) and 3.4 h (December, $k = 5.5 \times 10^{-5}\,s^{-1}$). Only negligible phototransformation took place in aerated organic solvents (methanol, acetonitrile or hexane) as well as in water in the absence of oxygen. Cox et al. [7] reported that the direct photolysis of metamitron producing deaminometamitron as a main product was slower in aqueous suspensions of soil particles, apparently due to their screening effect. Sancho et al. [8,9] studied phototransformation of metamitron in the presence of copper(II) and lead(II) salts. They caused a decrease in the rate of photodegradation by 15 and 13%, respectively.

Photocatalytic processes for a pesticide remediation in soils and water were summarized by Muszkat [10]. Suspended or immobilized TiO_2 was widely used as a photocatalyst. It was found that pesticides of various classes such as triazines, phenyl ureas and phosphororganics can be effectively destroyed utilizing photocatalysis on TiO_2.

In this paper, TiO_2 was used as a photocatalyst for degradation of a 1,2,4-triazine herbicide metamitron. A photocatalytic reaction was performed in two different types of photoreactors: (i) a photoreactor with a layer of TiO_2 P25 (Degussa) immobilized on a glass plate and (ii) a tube photoreactor containing colloidal solution of quantum sized TiO_2 particles (Q-TiO_2). It was found that direct photolysis participated in the overall photodegradation process. Main products of both photocatalytic degradation and direct photolysis were identified. The efficiency of both processes was compared.

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2. Experimental

2.1. Chemicals and solvents

TiO_2 powder (P25, Degussa, anatas:rutile = 80:20) was used for preparation of the TiO_2 layers. Colloidal solutions of TiO_2 were prepared using $TiCl_4$ (Fluka). Metamitron was isolated by extraction from a commercially available pesticide GOLTIX WP 70 (Bayer Vital GmbH) and recrystalized from ethanol [12]. TLC chromatography of metamitron and its photodegradation products was performed on a Silikagel Merck Kieselgel 60 GF_{254} plate using methanol and chloroform as solvents (both Lachema; Neratovice, Czech Republic) in a ratio of 1:9.

Acetonitrile, methanol and water (LiChrosolv®, solvents for chromatography) were purchased from Merck (Darmstadt, Germany).

2.2. Apparatus

2.2.1. Plate photoreactor with immobilized TiO_2 layer

The photoreactor (Fig. 1) was constructed from rectangular polymethylmethacrylate trays with two tanks at their ends [11]. The trays were sized to accommodate a glass plate (60 cm long and 30 cm wide) onto the surface of which a layer of TiO_2 photocatalyst was prepared. The whole assembly was supported by a rig with adjustable pins to allow an adjustment of the apparatus in an angle (α) of 10° towards to the horizontal position. A holder of three ultraviolet sun bed tubes (Osram Eversun L40W/79K) was placed 12 cm above the glass plate with the TiO_2 layer. The distance between the single sun bed tubes was 10 cm.

An aqueous solution of metamitron was pumped from a four-liter holding tank employing a centrifugal pump P (Nova, Sicce, Italy) to a higher tank. The flow was controlled with a valve in a pipe. The flow rate was measured using a Venturi tube V connected to a mercury-filled manometer. The overflow of solution from the higher tank formed a thin liquid film flowing over the glass plate with the fixed TiO_2 photocatalyst. The irradiated solution was collected in the lower tank and returned into the holding tank, i.e. the purified solution was recycling during the whole experiment. Samples were taken from the holding tank after certain irradiation times.

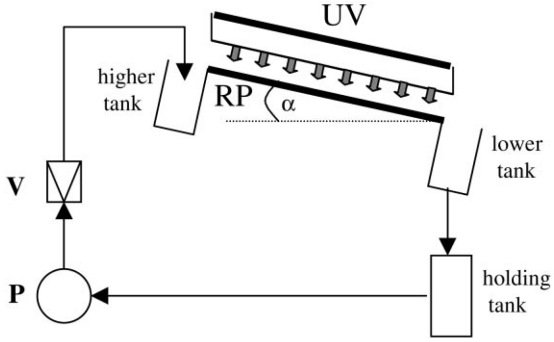

Fig. 1. Schematic representation of the batch mode plate photoreactor with the recycling flow of the solution. P: pump; V: Venturi tube; RP: a reactor plate 30 cm × 60 cm (width × length), α: inclination angle (10°); UV: a source of UV light (three parallel sunbed tubes L40W/79K).

Photon flux on the glass plate of this photoreactor was determined employing chemical actinometry. Using the potassium ferrioxalate actinometer [12], a mean value of 8.0×10^{-9} Einstein $cm^{-2} s^{-1}$ was obtained applying a quantum yield of 1.21.

The same photoreactor was also used for a separate investigation of the direct photolysis of metamitron. However, the TiO_2 layer was omitted from the glass plate in this case.

2.2.2. Tube photoreactor with Q-TiO_2 particles

The tube photoreactor is schematically shown in Fig. 2. It worked in a batch mode. Two coaxial quartz tubes were placed inside a steel cylinder. The inner quartz tube (a diameter of 24 mm, a length of 300 mm) was filled with the test solution (generally, an aqueous solution of metamitron or another organic pollutant; plus the colloidal particles of Q-TiO_2) and stirred by a magnetic stirrer during the whole experiment. Distilled water circulating between the inner and the outer quartz tube was kept at 20°C. Three medium pressure mercury lamps ("black light" lamps RVU, 125 W, Tesla Holešovice, Czech Republic), symmetrically placed around the outer quartz tube, were employed as a source of UV irradiation ($\lambda = 365$ nm). The inner surface of the steel cylindrical housing was covered by aluminum foil to ensure multiple reflection. An initial volume of 70 ml of the reaction mixture was applied in all experiments. Using the potassium ferrioxalate actinometer and applying the quantum yield of 1.21, a value of 4.9×10^{-5} Einstein $dm^{-3} s^{-1}$ was obtained for an input light intensity.

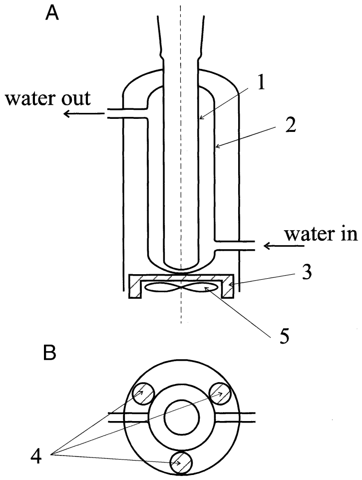

Fig. 2. Schematic representation of the batch mode tube photoreactor. (A) Longitudinal section; (B) transverse section; 1: inner quartz tube; 2: outer quartz tube; 3: magnetic stirrer; 4: UV lamps; 5: ventilator.

2.3. *Preparation of TiO_2 photocatalyst*

2.3.1. *Immobilized layer of TiO_2*

The photocatalyst layer was prepared by repeating sedimentation of TiO_2 P25 (Degussa) from its slightly acidic suspension ($10\,g\,l^{-1}$, pH $= 3$) onto a glass plate. The procedure was published by Bockelmann [13] and it was described in detail in our previous work [14].

2.3.2. *Q-TiO_2 particles*

Colloidal solutions of Q-TiO_2 particles were prepared by hydrolysis of titanium tetrachloride. 3.5 ml were added into 900 ml of well-mixed re-distilled water cooled to 1°C. The ionic strength of the resultant colloidal solution was lowered by transferring a part of the available HCl into re-distilled water via dialysis. A dialysis tubing–visking membrane with a size of 9–36/32 in. (Medicell International Ltd.) was used for this purpose. The process was finished when a pH value of 2.5 was reached. As described in [15], the Q-TiO_2 particles prepared by this procedure had a crystalline form of anatase.

2.3.3. *Analytical procedures*

The concentration of metamitron and the products of its photocatalytic and photolytic degradation were determined by HPLC technique. The HPLC analyses were carried out employing a Merck–Hitachi chromatographic set with absorption detection at 306 nm. As a mobile phase, mixture of acetonitrile and water (18:82 v/v) was applied with a flow rate of $1\,ml\,min^{-1}$. A LiChrosphere 100 RP-18 (5 μm) column (a length of 12.5 cm) equipped with a LiChroCART 4-4, RP-18 (5 μm) guard column (both of Merck, Germany) was used. For a better separation of intermediates, mobile phase in a ratio of methanol:water (30:70 v/v) was applied.

^1H and ^{13}C NMR spectra (δ, ppm; J, Hz) were measured with a spectrometer Varian Unity 200 (200.057 MHz for ^1H and 50.306 MHz for ^{13}C).

2.4. *Isolation of products of photodegradation of metamitron*

To isolate and identify products of photodegradation of metamitron, the plate photoreactor was employed. An aqueous solution of metamitron with an initial concentration of $10^{-3}\,mol\,l^{-1}$ was irradiated for 10 h. The course of the photodegradation was followed by HPLC applying the mobile phase methanol:water (30:70 v/v). In the first half-hour of this experiment, the samples were taken after each 5 min, following half-hour, sampling was after 10 min and then samples were taken each 30 min for next 3 h. All samples after 4 h of the experiment were taken after 1 h. Besides the starting metamitron (retention time of 5.94 min), seven photoproducts with retention times of 1.60, 2.02, 2.76, 3.53, 4.35, 8.48 and 10.79 min were found in the reaction mixture.

Evaporation of water under vacuum was the first step of isolation of the products from the reaction mixture. The solid remainder was extracted to acetonitrile, filtered and evaporated. An amount of 0.2 g of solid state was obtained and subsequently dissolved in 5 ml of chloroform. The solution was deposited on a start of a preparative TLC plate with 25 g of silica gel. A mixture of methanol:chloroform in a ratio of 1:9 was used for development.

3. Results and discussion

3.1. *Identification of products of photodegradation of metamitron*

Four main components **1**, **2**, **3** and **4**, corresponding to HPLC peaks with retention times 5.94, 4.35, 3.53 and 8.48 min were isolated after separation by TLC chromatography. The component **1** was shown to be the starting metamitron after a comparison of their TLC and HPLC retention times. To identify the other three components, their mass (MS) and NMR spectra were measured.

3.1.1. *Component 2*

Identified as deaminometamitron (6-phenyl-3-methyl-1,2,4-triazin-5(4H)-one).

MS: A molecular ion with a *m/z* of 187 (corresponding to formula $C_{10}H_9N_3O$) and fragments with a *m/z* of 104 (corresponding to formula C_7H_6N — protonated benzonitrile) and 42 were found.

NMR — ^1H *NMR* δ_{DMSO}: 2.33 s, 3H (CH_3); 7.42 m, 3H (H-3′, 4′, 5′); 8.14 m, 2H (H-2′, 6′); 10.98 bs, 1H (NH).

^{13}C *NMR* δ_{DMSO}: 21.3q (CH_3); 127.9 d, 128.4 d, 129.0 d (C-2′–6′); 135.2 s (C-1′); 148.7 s (C-6); 162.1 s (C-3); 162.6 s (C-5).

3.1.2. *Component 3*

Identified as deaminohydroxymetamitron (6-(2′-hydroxyphenyl)-3-methyl-1,2,4-triazin-5(4H)-one).

MS: A molecular ion with *m/z* of 203 (corresponding to formula $C_{10}H_9N_3O_2$) and a main fragment with *m/z* of 120 (corresponding to formula C_7H_6NO — protonated hydroxybenzonitrile) were found.

NMR — ^1H *NMR* δ_{DMSO}: 2.35 s, 3H (CH_3); 3.50 bs (H_2O, OH, NH); 6.81 dd, 1H, $J_1 = 8$, $J_2 = 1.5$ (H-3′); 6.84 ddd, 1H, $J_1 = 7.4$, $J_2 = 7.9$, $J_3 = 1.5$ (H-5′); 7.25 ddd, 1H, $J_1 = 7.4$, $J_2 = 8$, $J_3 = 1.7$ (H-4′); 8.05 dd, 1H, $J_1 = 7.9$, $J_2 = 1.7$ (H-6′).

^{13}C *NMR* δ_{DMSO}: 23.0 q (CH_3); 118.1 d (C-3′, 5′); 125.0 s (C-1′); 130.0 d and 130.3 d (C-4′ and 6′); 140.3 s (C-6); 150.5 s (C-2′); 158.6 s (C-3); 164.0 s (C-5).

3.1.3. *Component 4*

Identified as hydroxymetamitron (4-amino-6-(2′-hydroxyphenyl)-3-methyl-1,2,4-triazin-5(4H)-one).

MS: A molecular ion with *m/z* of 18 (corresponding to formula $C_{10}H_9N_4O_2$) and a fragment with *m/z* of 120 (corresponding to formula C_7H_6NO — protonated hydroxybenzonitrile) were found.

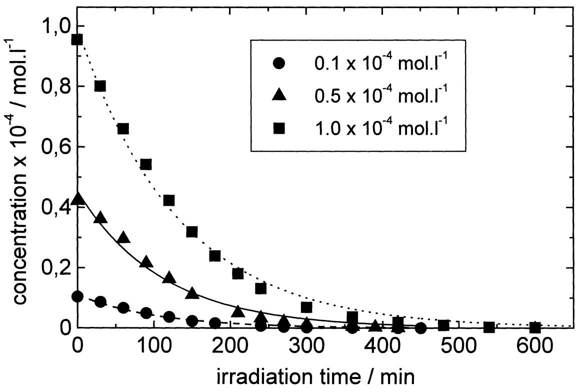

Fig. 3. Dependence of the metamitron concentration on the irradiation time during the photodegradation in the plate photoreactor for various initial concentration of metamitron.

NMR — ^1H *NMR* δ_{DMSO}: 2.44 s, 3H (CH_3); 5.85 s, 2H (NH_2); 6.95 ddd, 1H, $J_1 = 7.4$, $J_2 = 8.2$, $J_3 = 1.5$ (H-5′); 7.01 dd, 1H, $J_1 = 8.2$, $J_2 = 1.5$ (H-3′); 7.39 ddd, 1H, $J_1 = 7.4$, $J_2 = 8.2$, $J_3 = 1.5$ (H-4′); 8.10 dd, 1H, $J_{1'} = 8.2$, $J_2 = 1.5$ (H-6′); 11.62 bs, 1H (OH).

^{13}C *NMR* δ_{DMSO}: 18.8 q (CH_3); 116.8 d (C-3′); 118.7 d (C-5′); 124.0 s (C-1′); 130.4 d and 131.8 d (C-4′ and 6′); 144.6 s (C-6); 152.3 s (C-2′); 153.4 s (C-3); 157.9 s (C-5).

Based on the identified structures, a reaction scheme of phototranformations of metamitron was proposed (Fig. 7).

3.2. Photodegradation in the plate photoreactor

Kinetics of phototransformation of metamitron for its various initial concentrations was studied in the plate photoreactor. Corresponding time profiles are shown in Fig. 3. It can be seen that metamitron with the initial concentrations of 10^{-5}, 5×10^{-5} and 10^{-4} mol l^{-1} was totally degraded after 240, 360 and 600 min of irradiation, respectively. The decrease of metamitron concentration with irradiation time followed approximately first-order kinetics (see the fitted curves in Fig. 3). Corresponding rate constants are summarized in Table 1. They are slightly increasing with decreasing initial concentration (three times in the concentration range from 10^{-3} to 10^{-5} mol l^{-1}). Previous results for photodegradation of diuron using the same photoreactor indicated that rate constants did not depend on the initial concentration of diuron [11]. However, the investigations with diuron were carried out for lower initial concentrations.

Table 1
Rate constants of the photodecomposition of metamitron ($k_{d,MM}$) and of formation ($k_{f,DAMM}$) and decomposition ($k_{d,DAMM}$) of deaminometamitron in the plate photoreactor for various initial concentrations of metamitron (c_{MM})

c_{MM} (mol l^{-1})	TiO_2 layer	$k_{d,MM}$ (s^{-1})	$k_{f,DAMM}$ (s^{-1})	$k_{d,DAMM}$ (s^{-1})
1×10^{-5}	Yes	1.8×10^{-4}	2.7×10^{-5}	2.3×10^{-4}
5×10^{-5}	Yes	1.5×10^{-4}	2.4×10^{-5}	1.8×10^{-4}
1×10^{-4}	Yes	1.3×10^{-4}	1.7×10^{-5}	1.3×10^{-4}
1×10^{-3}	Yes	4.3×10^{-5}	1.1×10^{-5}	1.8×10^{-5}
1×10^{-4}	No	5.3×10^{-6}	5.2×10^{-6}	1.4×10^{-7}

The intermediates, deaminometamitron (component **2**) and hydroxymetamitron (**4**) showed time profiles typical for primary products. Deaminohydroxymetamitron (**3**) was a secondary product. Deaminometamitron was expected to be a main product of the direct photolysis of metamitron [6–9]. To determine a rate constant corresponding to the direct photolysis of metamitron, irradiation experiments in the same photoreactor with no TiO_2 layer immobilized on the glass plate were carried out. Other conditions were the same as for the photocatalytic experiments (initial concentration of 10^{-4} mol l^{-1}). While metamitron was completely decomposed in the presence of TiO_2 layer within 6 h, in the absence of the photocatalyst 20% still remained in reaction mixture after 16 h of irradiation. A first-order rate constant of the metamitron disappearance using the TiO_2 layer was six times higher than a corresponding value in the absence of the TiO_2 layer. This indicates that the direct photolysis represented only about 20% of the whole phototransformation of metamitron in the plate photoreactor.

A difference was also observed in the kinetics of formation and subsequent decomposition of deaminometamitron. A model of consecutive reactions of the first-order was applied

$$-\frac{\mathrm{d}c_{\mathrm{MM}}}{\mathrm{d}t} = k_{\mathrm{d,MM}}\, c_{\mathrm{MM}} \tag{1}$$

$$\frac{\mathrm{d}c_{\mathrm{DAMM}}}{\mathrm{d}t} = k_{\mathrm{f,DAMM}}\, c_{\mathrm{MM}} - k_{\mathrm{d,DAMM}}\, c_{\mathrm{DAMM}} \tag{2}$$

In Eqs. (1) and (2), c_{MM} and c_{DAMM} represent the concentration of metamitron and deaminometamitron, respectively. Symbols $k_{d,MM}$, $k_{f,DAMM}$ and $k_{d,DAMM}$ indicate the rate constants of decomposition of metamitron and of formation and decomposition of deaminometamitron. In the presence of the TiO_2 layer, the concentration of deaminometamitron reached a maximum at about 150 min of irradiation and then underwent further decomposition. After 10 h, no deaminometamitron was found in the reaction mixture. In the absence of the TiO_2 layer, only the formation of deaminometamitron without its consecutive disappearance was observed (Fig. 4).

3.3. Photodegradation in the tube photoreactor

The phototransformation of metamitron was also studied in the tube photoreactor in the presence and in the absence of the Q-TiO_2 particles. The products of photodegradation were found to be the same as in the case of the plate photoreactor, i.e. deaminometamitron (component **2**), hydroxymetamitron (**4**) and deaminohydroxymetamitron (**3**). The kinetics of disappearance of metamitron was examined as a function of various parameters: pH, concentration of the Q-TiO_2 particles and initial concentration of metamitron.

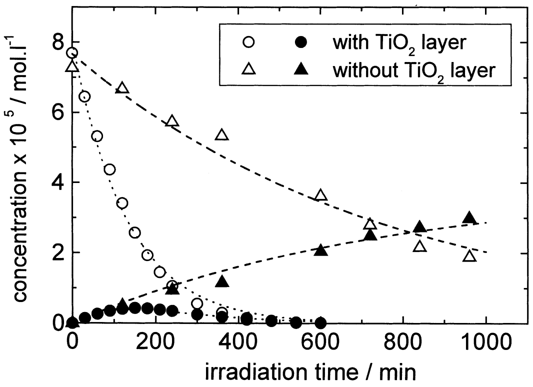

Fig. 4. Dependence of the concentration of metamitron (open symbols) and of the concentration of deaminometamitron (solid symbols) on the irradiation time during the phototransformation in the plate photoreactor in the presence (circles) and in the absence (triangles) of the TiO_2 layer.

Concerning pH, the Q-TiO_2 particles tend to coagulate at higher pH values [10]. Therefore, all experiments were performed in a narrow pH range from 1.9 to 2.7. The values of rate constants calculated according to the first-order kinetics were similar, i.e. no significant influence of pH on the reaction rate was found in this pH range. (Table 2).

In contrary to expectation, an increase in the concentration of TiO_2 particles led to a slower reaction rate of the metamitron disappearance. Corresponding rate constants are given in Table 2. To understand these results, irradiation experiments in the absence of the Q-TiO_2 particles were also performed. Rate constants corresponding to the direct photolysis of metamitron were found to be about five times higher than those measured in the presence of the Q-TiO_2 particles (compare in Table 2).

The first-order rate constant of the direct photolysis of metamitron decreased when pH value was increased to 6.4. However, when the pH value was adjusted to 10.4 using a borate buffer, the reaction rate of the metamitron disappearance again accelerated probably due to base catalyzed hydrolysis of metamitron observed in this pH range [2].

Table 2
Rate constants of the photodecomposition of metamitron ($k_{\mathrm{d,MM}}$) and of the formation ($k_{\mathrm{f,DAMM}}$) and the decomposition ($k_{\mathrm{d,DAMM}}$) of deaminometamitron in the tube photoreactor for various initial concentrations of Q-TiO_2 particles ($c_{\mathrm{TiO_2}}$) and various pH values (an initial concentration of metamitron was 10^{-4} mol l^{-1})

$c_{\mathrm{TiO_2}}$ (mol l^{-1})	pH	$k_{\mathrm{d,MM}}$ (s^{-1})	$k_{\mathrm{f,DAMM}}$ (s^{-1})	$k_{\mathrm{d,DAMM}}$ (s^{-1})
1×10^{-5}	1.90	2.2×10^{-3}	1.0×10^{-3}	8.1×10^{-5}
3.33×10^{-5}	1.90	1.2×10^{-3}	7.2×10^{-4}	7.2×10^{-5}
1×10^{-4}	1.90	7.2×10^{-4}	4.1×10^{-4}	3.4×10^{-5}
0	1.90	3.3×10^{-3}	1.8×10^{-3}	1.4×10^{-4}
1×10^{-4}	2.17	8.4×10^{-4}	3.0×10^{-4}	7.5×10^{-5}
0	2.17	3.5×10^{-3}	1.7×10^{-3}	1.6×10^{-4}
1×10^{-4}	2.70	8.2×10^{-4}	3.8×10^{-4}	7.2×10^{-5}
0	2.70	3.9×10^{-3}	1.9×10^{-3}	8.0×10^{-5}
0	6.40	1.7×10^{-3}	0.8×10^{-3}	4.5×10^{-5}
0	10.1	2.1×10^{-3}	1.0×10^{-3}	6.1×10^{-4}

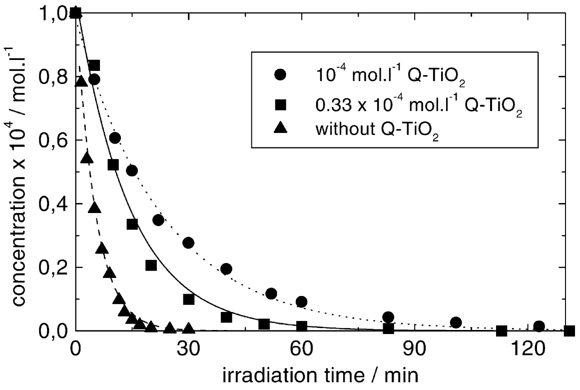

Fig. 5. Dependence of the concentration of metamitron on the irradiation time in the tube photoreactor for the concentration of the Q-TiO_2 particles; 10^{-4} mol l^{-1}, 0.33×10^{-4} mol l^{-1} and without Q-TiO_2 particles. An initial concentration of metamitron was 10^{-4} mol l^{-1} and pH of 1.9.

As was shown, the phototransformation of metamitron proceeded faster in the absence than in the presence of Q-TiO_2. The corresponding reaction rates increased with decreasing concentration of Q-TiO_2 (Fig. 5). These facts indicated that a competitive absorption of UV light between the Q-TiO_2 particles and the molecules of metamitron took place. Absorption spectra of both colloidal solution of the Q-TiO_2 particles (10^{-2} mol l^{-1}) and aqueous solution of metamitron (10^{-4} mol l^{-1}) are shown in Fig. 6 together with an emission spectrum of the light source used in the tube photoreactor. A comparison of these absorption spectra indicated that the light intensity originally absorbed by metamitron decreased significantly when Q-TiO_2 particles were added to the metamitron solution. The observed decrease of the reaction rate of disappearance of metamitron implies that the quantum yield of the direct photolysis of metamitron had to be higher than that of its photocatalytic degradation on TiO_2. Therefore, the reaction rate of the photocatalysis of metamitron was slower than the reaction

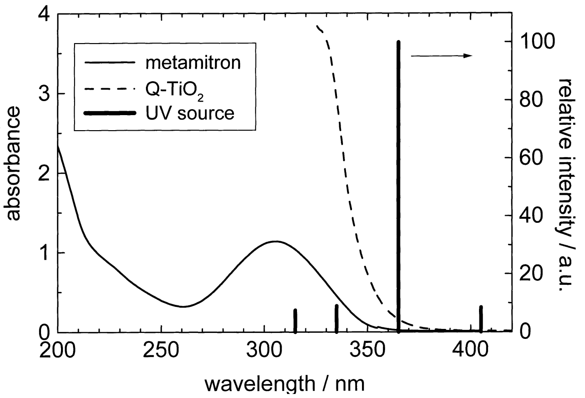

Fig. 6. Absorption spectra of aqueous solutions of metamitron (10^{-4} mol l^{-1}) and of the Q-TiO_2 particles (10^{-2} mol l^{-1}) measured in a 1-cm cell and an emission spectrum of the UV source used in the tube photoreactor.

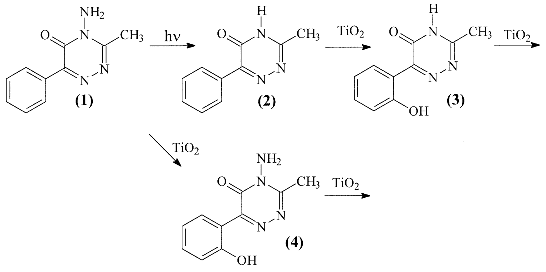

Fig. 7. Proposed reaction scheme of the phototransformations of metamitron (**1**) to deaminometamitron (**2**), deaminohydroxymetamitron (**3**) and hydroxymetamitron (**4**).

rate of its direct photolysis. That is why the decomposition of metamitron was suppressed by an addition of the Q-TiO_2 particles.

4. Conclusions

A reaction scheme of the photodegradation processes taking place in both photoreactors is proposed in Fig. 7. In the plate photoreactor, only about 17% of the whole amount of metamitron (component **1**) were decomposed by direct photolysis to deaminometamitron (**2**). The other 83% were transformed by the photocatalysis on the TiO_2 layer to hydroxymetamitron (**4**). This value corresponded well with the observed ratio (85:15) between the rate constants of the decomposition of metamitron (**1**) and the formation of deaminometamitron (**2**). It was observed that both deaminohydroxymetamitron (**3**) and hydroxymetamitron (**4**) consecutively disappeared. It means that the photodegradation continued beyond the structures listed in Fig. 7. However, the next products were not detected by HPLC with absorption detection, most probably due to their low concentration.

The situation was different in the tube photoreactor where approximately the half of metamitron (**1**) was phototransformed to deaminometamitron (**2**) in the presence of Q-TiO_2 particles. In contrary to the plate photoreactor, a competition in absorption of UV light between Q-TiO_2 and metamitron occurred in the tube photoreactor. A higher efficiency of homogeneous direct photolysis was the reason why this process dominated in the overall phototransformation of metamitron in the colloidal solutions of the Q-TiO_2 particles.

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