

The photodegradation of model quinolone carboxylates in aqueous media

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Abstract: This work was focused on the study of photoinduced processes of quinolone carboxylates in the presence of titanium dioxide in an alkaline media. UVA irradiation without/with titanium dioxide caused the decomposition of molecules, with higher efficiency of degradation in the presence of titanium dioxide. EPR spin trapping experiments proved that investigated quinolone carboxylates behave as the efficient scavengers of hydroxyl radicals produced upon irradiation of aerated alkaline titanium dioxide systems.

Keywords: Quinolone carboxylate, Titanium dioxide, EPR spectroscopy, UV/vis spectroscopy, EPR spin trapping technique

Introduction

Titanium dioxide nanoparticles are widely used mainly in paints and varnishes as well as paper and plastics. They are also applied in cosmetics and skin care products due to the ability of TiO₂ to absorb UV light. Titanium dioxide also represents one of the most efficient photocatalyst; upon supra-band gap irradiation of titanium dioxide particles photo-generated charge carriers are formed, positive holes (h⁺) in the valence band and negative electrons (e⁻) appear in the conduction band of TiO₂ semiconductor. After a separation, the photogenerated holes and electrons may be involved in redox processes at the titania surface. Positive holes are trapped by surface hydroxyl groups forming reactive hydroxyl radicals, ·OH, in aqueous media or initiate the direct oxidation of substrates. In oxygenated TiO₂ systems dissolved oxygen serves as a very effective electron acceptor, producing superoxide radical anions, O₂⁻. In aqueous titania suspensions superoxide radical anions may act as oxidizing agents or as an additional source of hydroxyl radicals *via* the subsequent formation of hydrogen peroxide, H₂O₂. Consequently, the exposure of titanium dioxide particles in oxygenated aqueous media resulted in the generation of short-lived reactive oxygen species (ROS), such as hydroxyl radical, superoxide radical anion or singlet oxygen (Fujishima, 2008; Hoffmann et al., 1995; Serpone and Pelizzetti, 1989; Dodd et al., 2011).

Recent investigations of photocatalytic processes on titanium dioxide are mainly focused on the elimination of hazardous pollutants from the water and the air. Many pharmaceutical compounds, espe-

cially antibiotics frequently present in wastewater, are classified as substances that are able to cause damages to the environment. Natural degradation of antibiotics is limited, so alternative ways of degradation have to be found. One possibility is heterogeneous photocatalysis based on titanium dioxide, which offers possible pathway for the elimination of organic substances at low concentrations *via* oxidative degradation to H₂O, CO₂ and mineral compounds (An et al., 2011; Blažková et al., 2000; Brezová and Staško, 1994; Brezová et al., 1994; Calza et al., 2008; Haque and Muneer, 2007; Kanakaraju et al., 2014; Lam et al., 2014; Li et al., 2012; Marona and Schapoval, 2001; Nasuhoglu et al., 2012; Nieto et al., 2008; Oller et al., 2011; Palominos et al., 2008; Paul et al., 2007; Paul et al., 2010; Phillips et al., 1990; Santoke et al., 2009; Sturini et al., 2012; Van Doorslaer et al., 2012; Van Wieren et al., 2012; Watkinson et al., 2007). The *N*-heterocyclic molecules upon UVA or visible irradiation could behave also as photosensitizers. In the aerated systems containing e.g. quinolones, fluoroquinolones, selenadiazoloquinolones, the formation of reactive oxygen species was confirmed and the consecutive reaction of ROS with quinolone can initiate their degradation (Albini and Monti, 2003; Barbieriková et al., 2011; Barbieriková et al., 2013; Santoke et al., 2009). Recent research was focused on the decomposition of drugs applied in medical treatment such as norfloxacin, ciprofloxacin, flumequine, levofloxacin, lomefloxacin or ofloxacin (An et al., 2010; An et al., 2011; Haque and Muneer, et al., 2007; Nieto et al., 2008; Oller et al., 2011; Paul et al., 2007; Van Doorslaer et al. 2013). For example, during the photocatalytic degradation of flumequine was

confirmed that hydroxyl radical and superoxide radical anion are involved into degradation (Nieto et al., 2008). Palominos et al. evaluated effect of radicals and scavengers in order to elucidate the paths involved in the photocatalytic degradation of flumequine (Palominos et al. 2008). Paul et al. were interested in photocatalytic decomposition of ciprofloxacin and analogous compounds in visible and UVA region (Paul et al. 2010). Van Doorslaer et al. gained a deeper insight of photocatalytic degradation mechanisms of moxifloxacin (Van Doorslaer et al. 2013). Haque and Muneer paid attention to the role of different types of titanium dioxide and they investigated the effect of TiO₂ structure on the photodegradation of norfloxacin in aqueous suspensions (Haque and Muneer, 2007). An et al. studied behaviour of norfloxacin, levofloxacin, as well as lomefloxacin and the absolute rate constants for hydroxyl radical and hydrated electron were reported. The application of scavengers indicates that holes are dominant reactive species and the hydroxyl radicals participate less in the photocatalytic degradation of moxifloxacin (An et al., 2010; An et al., 2011). Photocatalysis was chosen as a representative advanced oxidation technology (AOT) to degrade various types of fluoroquinolones. EPR spin trapping technique represents indirect method for detection of short-lived radicals, where the more stable spin adduct is formed after addition of radical species on spin trap molecule (Bačič et al., 2008; Brezová et al., 2007; Davies, 2002; Ouari et al., 2011). Our study was focused on the photodegradation of two model quinolone carboxylic acids **1** and **2** (Figure 1) without/with titanium dioxide upon UVA irradiation by utilization of UV/vis spectroscopy and EPR spin trapping technique with aim to determine the role of hydroxyl radicals in the process.

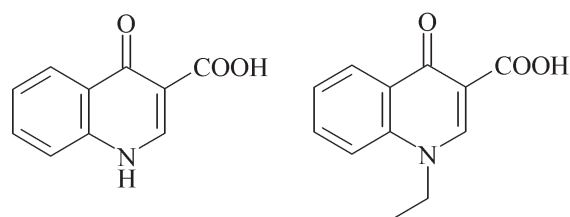


Fig. 1. Structures of 1,4-dihydro-4-oxoquinoline-3-carboxylic acid (**1**) and 1-ethyl-1,4-dihydro-4-oxoquinoline-3-carboxylic acid (**2**).

Experimental

Chemicals and reagents

The 1,4-dihydro-4-oxoquinoline-3-carboxylic acid (**1**) and 1-ethyl-1,4-dihydro-4-oxoquinoline-3-carboxylic

acid (**2**) were synthesized and purified as described in Černuchová et al. (Černuchová et al., 2004). Titanium dioxide P25 high surface (Degussa, Germany; non-porous anatase-rutile mixture with specific area of 75 m² g⁻¹) was used in all photocatalytic experiments. The sodium hydroxide was obtained from Mikrochem (Slovakia). The spin trapping agent 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) obtained from Sigma-Aldrich was distilled before application and stored at -18 °C. The concentrations of the photogenerated paramagnetic species were determined using solutions of 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO; Aldrich) as calibration standards. Alkaline medium was chosen due to better solubility of carboxylic acids. The concentration of stock solutions of **1** and **2** were 1 mM in sodium hydroxide (2 mM). Titania suspensions were prepared directly before measurements in redistilled water and carefully homogenized in an ultrasonic bath (Tesla, Slovakia). TiO₂ aqueous suspensions in concentration of 0.5 g L⁻¹ were used in experiments in photochemical immersion well; TiO₂ in concentration of 1.0 g L⁻¹ was used in EPR spin trapping experiments.

Experimental methods and apparatus

UV/vis spectroscopy

The UV/visible spectra were recorded using a UV-3600 UV/vis/NIR spectrophotometer (Shimadzu, Japan) with a square quartz cell (path length 10 mm, Cecil Instrument, Cambridge, England).

Photodegradation processes

in photochemical immersion well

The photodegradation processes were carried out at 303 K in a photochemical immersion well (Applied Photophysics, Great Britain) using a Pyrex sleeve for cutting off radiation below 300 nm. A 125-W medium-pressure mercury lamp (Applied Photophysics, Great Britain) was employed as the irradiation source. The temperature was regulated by ED-5 heating circulator (Julabo, Germany). The reaction system contained **1** or **2** in concentration 50 μM without/with titanium dioxide (concentration 0.5 g L⁻¹) in sodium hydroxide (1 mM). The solution/suspension was placed into the immersion well and systems containing titanium dioxide were left in dark for 30 minutes under slight stream of oxygen to extend the equilibrium between corresponding quinolone and titania. During exposure the reaction mixture was bubbled by molecular oxygen flow. Suspensions were centrifuged by Espresso (Thermo Electron Industries) for 15 minutes (at 14 500 RPM/min). The UV/vis spectra of samples were directly measured after their gathering.

EPR *in situ* photochemical experiments

The formation of paramagnetic intermediates upon monochromatic irradiation of suspensions was monitored *in situ* using an EPR spectrometer working in the X-band, EMX (Bruker, Germany). The reaction systems were prepared directly before measurement by mixing of 200 μL of titanium dioxide (1.0 g L^{-1}) with 25 μL of DMPO spin trapping agent (0.02 M) and carboxylic acids in range 200 μL – 0 μL ; 1 mM NaOH was added to total volume 425 μL . The prepared solutions were carefully bubbled by slight air stream and immediately transferred to a small quartz flat cell (WG 808-Q, Wilmad-LabGlass, USA; optical cell length 0.04 cm) optimized for the TE₁₀₂ cavity (Bruker Germany). The samples were irradiated at 295 K directly in the EPR resonator, and the EPR spectra recorded *in situ* during continuous photoexcitation (number of scan, NS = 2). As irradiation source served an HPA 400/30S lamp (400 W, Philips; the wavelengths below 300 nm were eliminated by a Pyrex filter with a thickness of 1 mm). The UVA irradiance of the UV lamp ($\lambda_{\text{max}} = 365 \text{ nm}$; 6 mW cm^{-2}) within the EPR cavity were determined using a UVX radiometer (UVP, USA). The concentration of photogenerated paramagnetic species was evaluated from double-integrated EPR spectra based on the calibration curve obtained by EPR spectra of TEMPOL solutions. Typical EPR settings for the series of photochemical experiments were following: center field, 335.0 mT; sweep width, 10 mT; gain, 1×10^6 ; modulation amplitude, 0.2 mT; microwave power, 10.03 mW; microwave frequency; 9.453–9.458 GHz, time constant, 20.48 ms; sweep time, 86 or 90 s. The g -value was determined within an uncertainty of ± 0.0001 by the simultaneous measurement of reference sample containing 2,2-

diphenyl-1-picrylhydrazyl (DPPH). EPR spectra obtained were analyzed and simulated by the Bruker software WinEPR and Winsim2002 software free available from the website of National Institute of Environmental Health Sciences (NIEHS) (<http://epr.niehs.nih.gov/>) (Duling, 1994).

Results and discussion

Photoinduced processes monitored by UV/vis spectroscopy

The electronic absorption spectra of **1**⁻ and **2**⁻ were measured in 1 mM NaOH (pH = 10.77 at 22 °C). The UV/vis spectrum of **1**⁻ shows absorption maxima at wavelengths of 324, 321, 300 (shoulder), 250 and 213 nm, typical for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The presence of ethyl group on the nitrogen on the 4-pyridone moiety causes only slight bathochromic shift of the absorption bands in UVA region. These observations are in the good accordance with the previous published data (Barbieriková et al., 2011).

Figure 2a represents the changes in electronic absorption spectra observed upon UVA exposure of **1**⁻ in 1 mM NaOH saturated by oxygen. During irradiation we have observed the decrease of absorption maxima at 324 nm, 321 nm, 250 nm and 231 nm. After 90 minutes of irradiation, the absorption spectrum showed two maxima at 207 nm and 255 nm and small increase of absorbance up to 360 nm (pale yellow solution after irradiation). The similar changes were monitored for the **2**⁻ (data not shown). Presence of titanium dioxide strongly affected the behaviour of the reaction system after the UVA exposure (Fig. 2b). Upon 7 minutes of irradiation no absorption was evidenced at UVA region in both reaction systems.

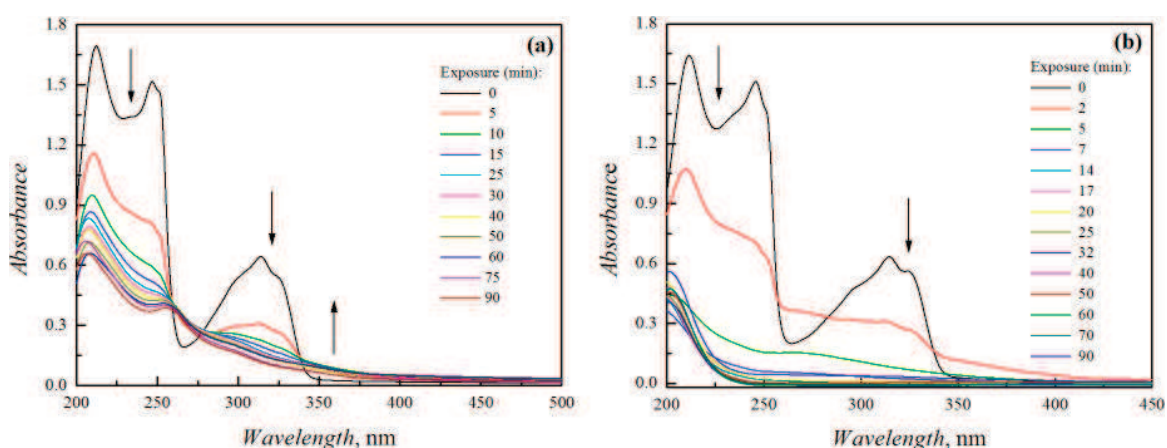


Fig. 2. Changes in electronic absorption spectra monitored upon continuous UVA irradiation of oxygenated **1**⁻ (a) without and (b) with titanium dioxide in 1 mM NaOH. Initial concentration: $c_0(\mathbf{1}^-) = 50 \mu\text{M}$; $c_0(\text{TiO}_2) = 0.5 \text{ g L}^{-1}$. Optical path length of quartz cell was 10 mm.

It was shown that molecules such as quinolones, fluoroquinolones, selenadiazoloquinolones behave as photosensitizers, and upon UVA exposure generate both singlet oxygen and superoxide radical anion (Albini and Monti, 2003, Barbieriková et al. 2011, Barbieriková et al. 2013, Santoke et al., 2009). Singlet oxygen is known as a strong oxidizing agent and is used as a reagent in a number of important chemical processes (Derosa, 2002). The superoxide radical anion in aqueous media converts to hydroxyl radical particle that is even more reactive than $O_2^{\cdot-}$ (Halliwell and Gutheridge, 2004). All these ROS may be involved in the oxidation processes with quinolones in the system. Simultaneously, since the (triplet) excited state of quinolones is highly oxidizing so the photoinduced oxidation of various anions occurs efficiently leading to the formation of various organic radicals. The reaction pathways of quinolone photodegradation processes are still under study; e.g. for fluoroquinolones it was confirmed, that first step of the photodegradation is a defluorination coupled with a decarboxylation and a side-chain degradation. For non-fluorinated quinolones the decarboxylation seems to be the main photoprocess upon UVA exposure (Albini and Monti, 2003). So we assume that the UVA exposure of **1**⁻ and **2**⁻ led to the generation of radical species coupled with their photodecarboxylation. The presence of titanium dioxide significantly changes the reaction route, and we suppose the more complex stepwise decomposition of quinolone carboxylates *via* hydroxyl radicals generated on the titania surface. The role of hydroxyl radicals as a crucial species in decomposition of organic compounds

in aquatic oxygenated media was confirmed (An et al. 2010; Blažková et al., 2000; Brezová and Staško, 1994; Brezová et al., 1994; Brezová et al., 2007; Dvoranová et al., 2002, Fujishima et al., 2008), so we focused our further attention on more detailed study of the role of their generation by applying EPR spin trapping technique in titanium dioxide suspensions.

Photoinduced processes monitored by EPR spectroscopy

The photoexcitation of titanium dioxide aerated in alkaline suspensions led to the formation of reactive oxygen species, mainly hydroxyl radicals (Fig. 3). Depending on the reaction conditions, the hydroxyl radicals can be scavenged by the organic substrate attending in the system.

Reaction of hydroxyl radical with a diamagnetic spin trap DMPO resulted in the formation of more stable paramagnetic spin adduct [•]DMPO-OH with EPR spectrum characterized in water by typical four-line signal with spin Hamiltonian parameters $a_N = 1.492$ mT; $a_H^{\beta} = 1.472$ mT; $g = 2.0057$ obtained from the simulation analysis. On the other hand, if the hydroxyl radical is scavenged in the competitive reactions by molecules **1**⁻ or **2**⁻, the EPR signal of [•]DMPO-OH decreased. Figure 4 represents the time-course of [•]DMPO-OH EPR spectra obtained upon continuous UVA irradiation of **1**⁻/TiO₂/DMPO/air containing different initial concentration of **1**⁻. The highest formation of [•]DMPO-OH was monitored for the reference system without **1**⁻ (Fig. 4a), with the increasing initial concentration of **1**⁻ the generation of [•]DMPO-OH was lower (Fig. 4b, c) and in the presence of 0.47 mM **1**⁻, no EPR signal was detected (Fig. 4d). The similar situation was monitored for the **2**⁻.

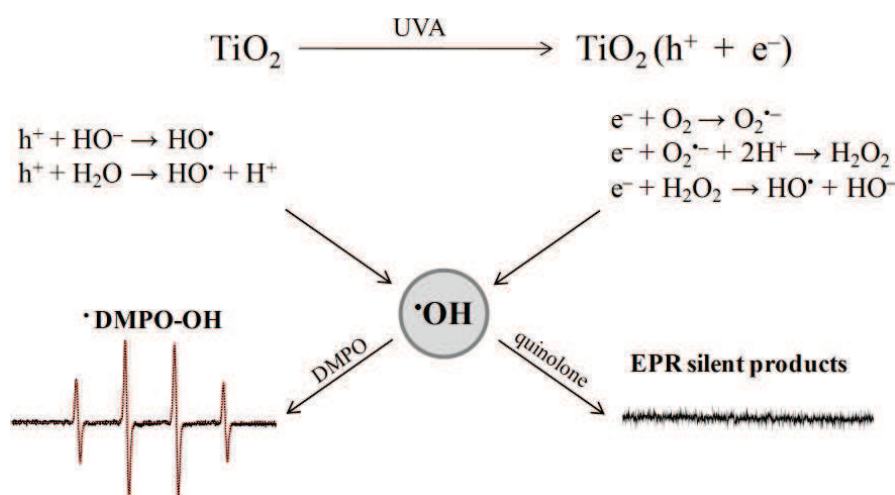


Fig. 3. Scheme of competitive scavenging of photogenerated hydroxyl radicals upon photoexcitation of titanium dioxide aqueous suspensions in the presence of DMPO spin trap and quinolone carboxylate.

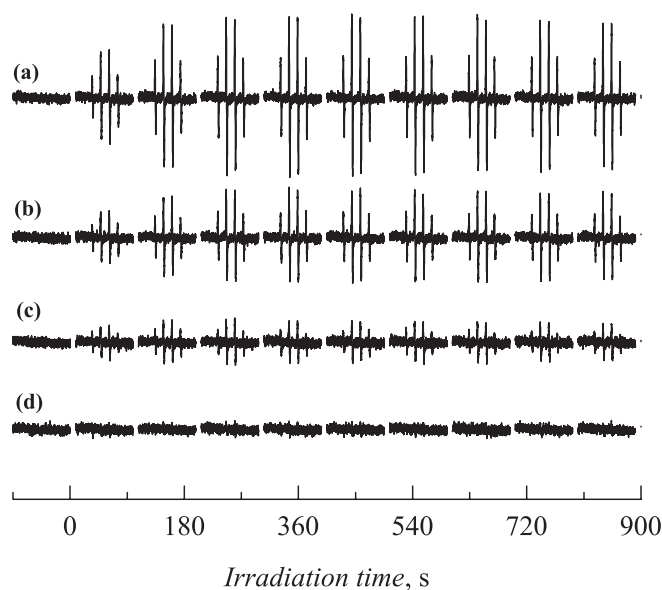


Fig. 4. Time-course of EPR spectra (SW = 10 mT) observed upon continuous UVA irradiation of I^- in aerated alkaline titanium dioxide suspensions in the presence of DMPO spin trap. Initial concentrations: $c_0(\text{TiO}_2) = 0.471 \text{ g L}^{-1}$, $c_0(\text{DMPO}) = 1.24 \text{ mM}$. Initial concentrations of I^- (in mM): (a) 0; (b) 0.059; (c) 0.235 and (d) 0.470. The first spectrum was measured without irradiation.

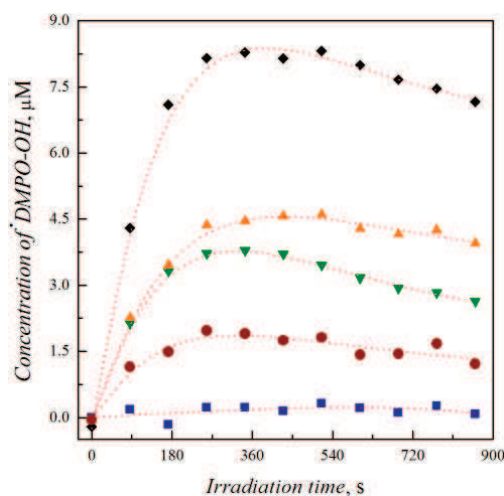


Fig. 5. Time-dependencies of $\cdot\text{DMPO-OH}$ spin adduct concentration observed upon continuous UVA irradiation of $\text{I}^-/\text{TiO}_2/\text{DMPO}/\text{air}$ suspensions with various initial concentration of I^- . Initial concentrations: $c_0(\text{TiO}_2) = 0.471 \text{ g L}^{-1}$, $c_0(\text{DMPO}) = 1.24 \text{ mM}$. Initial concentrations of I^- (in mM): \blacklozenge 0; \blacktriangle 0.047, \blacktriangledown 0.118; \bullet 0.235; \blacksquare 0.470. The symbols represent the experimental data and dashed lines their mathematical simulations using least squares analysis.

Figure 5 shows the time-dependencies of $\cdot\text{DMPO-OH}$ concentration (calculated from the corresponding EPR spectra depicted in Fig. 4) during irradiation of heterogeneous $\text{I}^-/\text{TiO}_2/\text{DMPO}/\text{air}$ systems in the presence of various initial concentrations of I^- .

The initial rates of $\cdot\text{DMPO-OH}$ formation, R_{in} , were calculated from experimental data and their dependencies on the initial concentration of quinolone. Plots of the initial rate of $\cdot\text{DMPO-OH}$ formation as a function of the initial concentration of the studied quinolones are shown in Fig. 6.

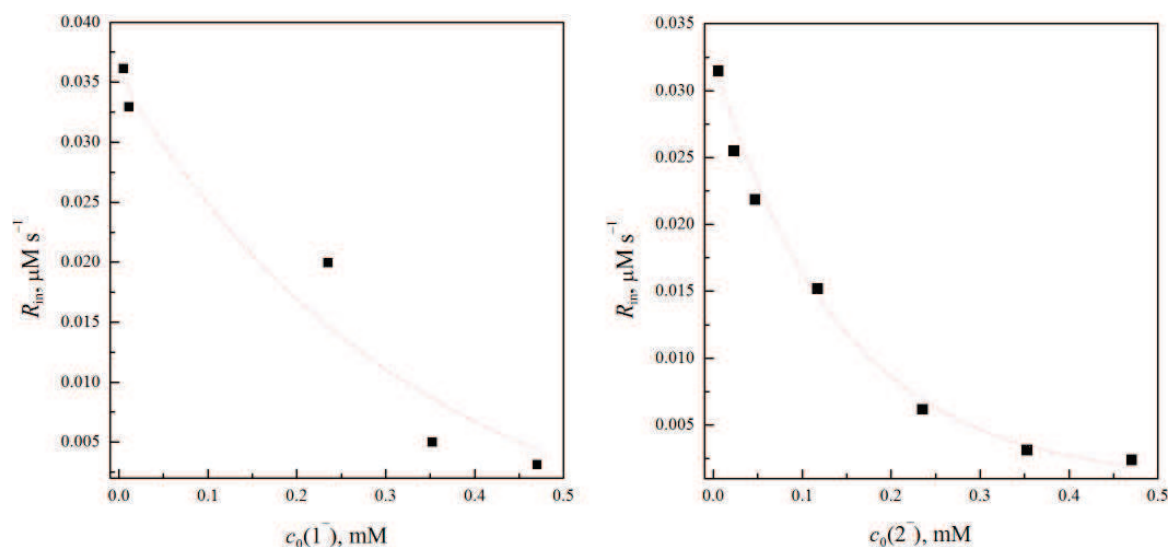


Fig. 6. Dependencies of the initial rate R_{in} of \cdot DMPO-OH formation on initial concentrations of quinolone carboxylates 1^- and 2^- in continuously irradiated aerated alkaline TiO_2 suspensions. Initial concentrations: $c_0(\text{TiO}_2) = 0.471 \text{ g L}^{-1}$, $c_0(\text{DMPO}) = 1.24 \text{ mM}$.

Initial rate of formation \cdot DMPO-OH spin adduct exponentially decreases with the higher concentration of 1^- and 2^- for both reaction systems. Although the reaction of the hydroxyl radical with DMPO is very fast in aqueous media ($k_{\text{DMPO}} = 3.4 \cdot 10^9 \text{ s}^{-1} \text{ M}^{-1}$ (Halliwell and Gutheridge, 2004)) and initial concentration of DMPO is significantly higher than quinolone carboxylate, under given experimental conditions the hydroxyl radicals are preferentially scavenged by the 1^- or 2^- (no \cdot DMPO-OH formation).

Under the given experimental conditions, only the information on \cdot DMPO-OH spin adducts formed could be received, no direct evidence on addition of hydroxyl radical to 1^- and 2^- is obtained. The formation of radical species in the heterogeneous system is more complicated comparing the homogeneous system. The origin of the reactive species formed upon UVA exposure in the photocatalytic system may varied. Some recent studies evidenced that oxidation of organic substances takes place directly on the photogenerated holes (primary oxidation) and quantum yield of free hydroxyl radicals formed is lower than photogenerated holes (Draper et al., 1990; Ishibashi et al., 2000; Tachikawa et al., 2004). It was also demonstrated that \cdot OH radicals formed by oxidation of the hydroxyl groups or adsorbed water on the semiconductor surface, play a role in the initiation of oxidation reactions of substances weakly adsorbed on the surface of TiO_2 (indirect oxidation) (Jaeger and Bard, 1979; Fujishima et al., 2008; Hoffmann et al., 1995). In photodegradation processes also another ROS, such as superoxide

radical anion or singlet oxygen, both formed in the presence of molecular oxygen, have to be considered. Superoxide radical anion is less reactive than hydroxyl radical, so it is less expected to be involved in the oxidation reactions but may serve as additional source of hydroxyl radicals (Fujishima et al., 2008; Hoffmann et al., 1995). Generation of singlet oxygen in irradiated TiO_2 suspensions was confirmed, but in the aqueous environment the lifetime of singlet oxygen due to its rapid deactivation of the surface of TiO_2 is extremely short ($\tau = 2 \mu\text{s}$) and is about five times lower than lifetime of hydroxyl radicals ($\tau = 10 \mu\text{s}$) or photogenerated holes (Nosaka et al., 2004). The pH of the environment is another important factor for the photocatalysis, which can affect the surface charge on the surface of the catalyst. Isoelectric point (zero zeta potential) of TiO_2 (P25) is at about $\text{pH } 6.0 \pm 0.5$. Thus, at more acidic $\text{pH} < 6$, the TiO_2 particle surface is positively charged, while at $\text{pH} > 6$, the surface is negatively charged, and will be attracted to the positively charged particles or particles with partial positive charge (Brezová et al., 1994). Under given experimental conditions, quinolone carboxylic acid in alkaline solution dissociates in the ions ($\text{RCOOH} \leftrightarrow \text{RCOO}^- + \text{H}^+$), meaning that the titania surface will be more attracted to the positive particles such as H^+ , Na^+ , and the DMPO spin trap (positive charge on the nitrogen). This mean that the photodegradation processes may proceed near the semiconductor surface.

The reaction pathway of organic substrate decomposition in the heterogeneous systems is more

complicated than in the homogeneous system due to simultaneous formation of ROS on the irradiated titanium dioxide as well as *via* photoexcitation of quinolones. We supposed that in our reaction systems all these species are involved in the processes resulted in the oxidation of the quinolone molecule.

Conclusions

Our study focused on the photochemical degradation of model quinolone compounds evidenced the formation of reactive oxygen species, mainly hydroxyl radicals, which are responsible for the decomposition of organic molecules. The results showed that the photocatalytic decomposition of quinolone carboxylates upon UVA irradiation is more complex and efficient in the presence of TiO₂ system in comparison with photoinduced processes in homogeneous solutions and represents an effective way of quinolone compounds elimination.

Acknowledgement

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