



Invited feature article

Effect of inorganic ions, photosensitisers and scavengers on the photocatalytic degradation of nicosulfuron

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ABSTRACT

In the present study, the photocatalytic degradation of nicosulfuron, using TiO₂ as a catalyst under UV light (315–400 nm), was studied. The optimization of the nicosulfuron photodegradation was performed. It was found that the optimal concentration of the catalyst was 1 g L⁻¹ at concentration of nicosulfuron solution of 20 mg L⁻¹ while the highest reaction rate was obtained using 2 g L⁻¹. The degradation rate was the highest at pH = 5.0. Effects of anions (Cl⁻, SO₄²⁻, NO₃⁻ and F⁻) and cations (Na⁺, Ca²⁺, Al³⁺) were investigated. In addition, the influence of isopropanol, acetone, and hydrogen peroxide was studied. It was shown that the photocatalytic degradation is mainly due to the reaction of nicosulfuron with •OH in solution.

Also, liquid chromatography coupled with mass spectrometry (HPLC–MS) was used to identify intermediates during the photocatalytic degradation of nicosulfuron. the mineralization was monitored with ion chromatography (IC) and total organic carbon (TOC) analysis. Although 100% HPLC removal of nicosulfuron was achieved, only 69% TOC removal after 90 min was recorded. The results of ion chromatography showed that the mineralization resulted in ammonium and nitrate ions during the process. The phytotoxicity experiments using mung bean seeds showed a reduction in phytotoxicity.

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1. Introduction

Due to their long-term persistence in soil, high water solubility and photochemical stability, contamination of water resources with organic chemicals (usually pesticides) used in agriculture is a cause of environmental concern [1]. The most frequently used pesticides in agriculture are amides, anilides, carbamates, phenylureas, organophosphorous derivatives, sulfonylureas and triazines. Along with other pesticides, sulfonylurea herbicides have gained attention due to their good crop selectivity, low application rates and favorable environmental properties.

Sulfonylurea herbicides are highly soluble in water, and have moderate to high mobility [2]. due to the slow degradation their use is not safe.

Nicosulfuron, 2-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfonyl)-N,N-dimethylnicotinamide (C₁₅H₁₈N₆O₆S), as a member of sulfonylurea herbicides, characterized by the presence of the

pyridine and pyrimidine rings connected with sulfonylurea bridge in the molecule is a selective systemic herbicide absorbed by the foliage and roots, with rapid translocation in xylem and phloem to the meristematic tissues [3]. Nicosulfuron can be classified as low to moderate persistent in soil (1st order DT₅₀ = 7–46.3 days) [4] with maximum residual level between 0.01 and 0.02 according to Reg. (EU) No 617/2014. Despite the low persistence of nicosulfuron, its residues have been reported in many materials, such as soil, surface waters, and some crops [5]. Sarmah and Sabadie [6] and Sabadie [5] studied the hydrolysis of sulfonylurea herbicides including nicosulfuron, and Sabadie [5] has found that hydrolysis of nicosulfuron is much more rapid under acidic conditions, while the reaction follows first-order kinetics. It was reported that nicosulfuron can be biodegraded by the bacteria, such as *Serratia marcescens* N80 [7].

Sulfonylurea herbicides have been a subject of different photodegradation studies. For example, Vulliet et al. [8–11] investigated TiO₂ photocatalytic degradation and photolysis of cinosulfuron and triasulfuron; Maurino et al. [12] studied TiO₂ photocatalytic degradation of chlorsulfuron and thifensulfuron methyl; and Benzi et al. [13]; studied photolysis of amidosulfuron.

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Two studies have reported photolysis of nicosulfuron: photo-induced aqueous degradation [2], and photolysis on a simulated cuticular wax film [14]. The photocatalytic degradation of five sulfonylurea herbicides, including nicosulfuron, using ZnO (with or without $\text{Na}_2\text{S}_2\text{O}_8$), WO_3 , SnO_2 and ZnS as photocatalysts under natural sunlight has been also investigated [15], as well as the photocatalytic degradation of 30 sulfonylurea herbicides including nicosulfuron with TiO_2 and ZnO tandem with $\text{Na}_2\text{S}_2\text{O}_8$ [16].

To the best of our knowledge, no detailed optimization study of the nicosulfuron photodegradation in the presence of TiO_2 and UV light has been published so far. In addition, the effect of inorganic anions and cations, alcohol, hydrogen peroxide and acetone was studied in order to get better insight in the mechanism of nicosulfuron photodegradation. Also, a HPLC–MS analysis of the photodegradation intermediates was performed. Total ion chromatograms in positive (PI) and negative (NI) ionization mode were recorded for the samples with the irradiation time ranging from 0 to 90 min and the evolution of intermediates was established. IC and TOC analysis were also used to monitor the nicosulfuron mineralization.

2. Materials and methods

2.1. Materials

Nicosulfuron, CAS RN 111991-09-4, (technical grade, 98.1%, Galenika-Fitofarmacija, Serbia) was applied without further purification. Titanium dioxide (TiO_2) P25 supplied by Evonik was used as a photocatalyst. Sodium chloride, sodium sulphate, sodium hydrogen carbonate, sodium nitrate, sodium fluoride, calcium sulphate, aluminium sulphate, isopropanol, hydrogen peroxide, sodium hydroxide, hydrochloric acid, acetonitrile, acetic acid, and sodium hypochlorite were obtained commercially. deionized water was obtained from a Milipore Waters Milli Q purification unit.

2.2. Methods

2.2.1. Photodegradation experiment

The photodegradation of nicosulfuron was investigated through the analysis of a series of solutions with a defined pesticide concentration and varying TiO_2 content. Reactions were performed in an open 250 cm^3 volume reactor, thermostated at 25°C . For irradiation an Osram ultra vitalux[®] 300 W lamp was used (mixture of lights UV-A:UV-B = 13.6:3). The lamp was placed 400 mm from the surface of the reaction mixture.

Typical experimental procedure: 100 ml of the solution was placed into the reactor and before the photodegradation experiment, the reaction mixture was stirred for 30 min in the dark. Continuous stirring was maintained through the reaction. Aliquots were taken at time intervals followed by filtration through Cronus 13 mm Nylon Syringe filters $0.2\text{ }\mu\text{m}$ in order to remove the suspended TiO_2 particles before the HPLC analysis. UV spectrophotometric analysis was performed on UV–vis 1800 Shimadzu spectrophotometer. The pH of the samples was adjusted by the addition of diluted NaOH or HCl solutions. When influence of $\text{Al}_2(\text{SO}_4)_3$ was investigated, $\text{Al}_2(\text{SO}_4)_3$ was added to nicosulfuron solution and then pH was adjusted. When it was necessary, solution was filtrated to remove any formed solids. After that, TiO_2 was added. Mettler Toledo FiveEasy pH Meter was used to monitor a pH of the samples. All the experiments were done in triplicate.

2.2.2. Analytical procedures

For HPLC determination, all samples were filtered through $0.20\text{ }\mu\text{m}$ syringe filters and were analyzed at 240 nm and at ambient temperature (25°C) on a SpectraSYSTEM P4000 liquid

chromatograph with a SpectraSYSTEM UV1000 detector, equipped with a reversed phase column type Zorbax SB C8 ($150\text{ mm} \times 4.6\text{ mm}$ i.d., $5\text{ }\mu\text{m}$ particle size). The mobile phase (flow rate 1.0 ml min^{-1}) was a mixture of acetonitrile and water (45:55, v/v) with 0.05% glacial acetic acid solution. Sample injection volume was $20\text{ }\mu\text{l}$ ($t_{\text{R}}(\text{nicosulfuron}) = 3.0\text{ min}$). The concentration of ions was monitored by ion chromatography (Dionex, ICS-3000), cation column IonPac CS16, eluent 30 mM MSA and anion column IonPac AS14A, eluent 8/1 mM ($\text{NaCO}_3/\text{NaHCO}_3$); flow rate 1 ml min^{-1} corresponding to the retention times: $t_{\text{R}}(\text{NO}_2^-) = 6.1\text{ min}$; $t_{\text{R}}(\text{NO}_3^-) = 8.3\text{ min}$; $t_{\text{R}}(\text{SO}_4^{2-}) = 14.5\text{ min}$; $t_{\text{R}}(\text{NH}_4^+) = 8.9\text{ min}$.

A PPM LAB TOC analyzer (Pollution & Process Monitoring Ltd.) was used for total organic carbon analyses.

2.2.3. HPLC–MS analysis

A Thermo Fisher Scientific (Waltham, MA, USA) apparatus was used: a vacuum solvent degassing unit, quaternary pump (Surveyor), a linear ion trap mass spectrometer (LTQ XL) with an electrospray interface, and the Xcalibur v.2.1 software package. the reverse phase Zorbax Eclipse[®] XDB-C18 column, $75 \times 4.6\text{ mm}$ i.d. and $3.5\text{ }\mu\text{m}$ particle size (Agilent Technologies, Santa Clara, CA, USA) was used for the separation of the analytes. A pre-column was also installed, $12.5 \times 4.6\text{ mm}$ i.d. and $5\text{ }\mu\text{m}$ particle size (Agilent Technologies, Santa Clara, CA, USA). The mobile phase consisted of water (A), acetonitrile (B), and 10% acetic acid (C). The gradient elution was used and the gradient changed as follows: 0 min, B 69%, C 1%; 20 min, B 29%, C 1%. The initial conditions were re-established and maintained for 15 min between injections. The mobile phase flow rate was 0.5 ml min^{-1} . In the HPLC system $10\text{ }\mu\text{L}$ of the extract was injected.

Both positive (PI) and negative ion (NI) modes were used during the analysis, while the mass spectra were recorded across the range 50–1000 m/z . The optimal source working parameters were: source voltage (5 kV), sheath gas (14 au, i.e., 14 arbitrary units), auxiliary gas (10 au), and capillary temperature (290°C).

2.2.4. Phytotoxicity testing

Phytotoxicity of the samples before and after the nicosulfuron degradation was examined using the mung bean seeds (*Vigna mungo*). The healthy and uniformly sized seeds were selected and surface sterilized with NaOCl (0.5%, 30 min). At the bottom of each sterilized glass Petri plate the filter paper and 10 mung bean seeds were placed. In the defined time intervals (12 h) the filter paper was wetted (3 ml) using the distilled water (control) and the appropriate samples (before and after degradation). The samples were incubated at room temperature for six days. After six days the radicle length was measured and the phytotoxicity of the samples was calculated using the following equation [17]:

$$\text{Phytotoxicity (\%)} = \frac{\text{Radicle length of control} - \text{Radicle length of sample}}{\text{Radicle length of control}} \times 100 \quad (1)$$

2.2.5. Statistical analysis

The curve fitting and statistical data were obtained using Origin version 8.0 statistical software.

3. Results and discussion

3.1. The optimization study

The nicosulfuron degradation was studied under different experimental conditions in order to investigate the adsorption of nicosulfuron on TiO_2 and compare the direct photolysis with

photocatalysis. Fig. 1 shows the typical degradation curves obtained by HPLC analysis under different conditions. The degree of nicosulfuron degradation was monitored by the normalized concentration (C/C_0) versus time (t), where C_0 is the initial and C is the current nicosulfuron concentration.

As it can be seen, there is no significant nicosulfuron degradation during direct photolysis: only 5% of the initial concentration was degraded (Fig. 1), which is in accordance with the study of Fenoll et al. [10], who obtained less than 10% of degradation during photolysis. As evident from Fig. 1, the presence of TiO_2 has a remarkable effect on the degradation rate. Approximately 100% of nicosulfuron was decomposed due to the photocatalysis, compared to the 5% observed under the photolysis conditions. All data were obtained using HPLC analysis since quantitative UV spectrophotometric analysis could not be applied. However, the changes of the UV absorption spectra of the nicosulfuron photocatalytic degradation are shown in Fig. S1 (Supplementary material). The decrease of the absorption peak implies the degradation of nicosulfuron.

It should be pointed out that before irradiation, the initial solutions were magnetically stirred in the dark for 30 min in order to reach the adsorption equilibrium [10], as it is presented in Fig. 1. The adsorption of nicosulfuron on TiO_2 was found to be less than 5%.

Since TiO_2 as a photocatalyst has a remarkable influence on the degradation rate during the photodegradation process, its concentration is one of the parameters which should be optimized. In this study, the initial TiO_2 concentration was varied in the range from 0.5 to 4 g L^{-1} . Fig. 2 shows the time-dependence of C/C_0 at different TiO_2 concentrations in the photocatalytic degradation process.

Additionally, as it is well known, the degradation rates of the photocatalytic oxidation of various organic contaminants over illuminated TiO_2 conformed to the Langmuir–Hinshelwood (L–H) kinetics model given in Eq. (2) [18]:

$$r = \frac{dC}{dt} = \frac{k \cdot K \cdot C}{1 + K \cdot C} \quad (2)$$

Where: r – is the oxidation rate of the reactant [$\text{mg L}^{-1} \text{min}^{-1}$]; k – is the reaction rate constant [$\text{mg L}^{-1} \text{min}^{-1}$]; and K is the adsorption coefficient of the reactant [L mg^{-1}].

Fig. 2. The photocatalytic degradation of nicosulfuron (20 mg L^{-1}) in the presence of different TiO_2 concentrations (g L^{-1}) at pH = 5.0: (■) 0.5; (□) 1; (○) 2; (△) 3 and (◇) 4. The insert represents the effect of TiO_2 concentration on the degradation rate.

At low concentrations of the organic pollutant, Eq. (1) can be transformed into a pseudo-first order equation (Eqs. (3) and (4)). the half time of the reaction can be obtained by using Eq. (5) [19,20].

$$\ln\left(\frac{C_0}{C}\right) = k \cdot t \quad (3)$$

$$C = C_0 \cdot e^{-k \cdot t} \quad (4)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (5)$$

Based on the results presented in Fig. 2 (insert), the concentration of TiO_2 strongly influences the reaction rate. It was found out that the highest reaction rate was achieved by using the TiO_2 concentration of 2 g L^{-1} . Below and above this

Fig. 1. The influence of different experimental conditions on nicosulfuron (20 mg L^{-1}) degradation at pH = 5.0: (□) adsorption of TiO_2 in the dark; (○) direct photolysis and (△) photocatalytic degradation in the presence of TiO_2 Evonik P25 (2 g L^{-1}). Insert: hydrolysis of nicosulfuron (20 mg L^{-1}) at pH 3.4 (■) and pH 5 (□); photolysis of nicosulfuron (20 mg L^{-1}) at pH 3.4 (○) and pH 5 (△).

concentration the reaction rate was lower. The pseudo-first order constant values are given in Table S1 (Supplementary material). On the contrary, from a practical point of view, the optimum value for the TiO_2 concentration should be 1 g L^{-1} . This optimum value of the TiO_2 concentration should correspond to the optimum of light absorption [11,21]. Besides light scattering, at higher concentrations, the agglomeration of TiO_2 particles can take place. This leads to the loss of the surface area which can absorb light and promote the reaction [22].

The pH of water which contains organic pollutants also has important influence on the photodegradation processes [23–26]. This effect is also present in the photocatalytic degradation of sulfonylureas [11,16], where it was found that the photodegradation was faster at lower pH values. In this study, the photodegradation of nicosulfuron was studied at four pH values (3.4, 5.0, 6.4 and 10.9). the time-dependence of C/C_0 at different pH values is presented in Fig. 3. Fig. 3 (insert) shows that the photodegradation rate increases with the increasing pH up to the value $\text{pH} = 5.0$, and after that, with increasing pH the rate of photodegradation decreases. As we have stated in the Introduction, Sabadie [5] has found that hydrolysis of nicosulfuron is much more rapid under acidic conditions: the reaction rate decreased as pH increased with the minimum at pH 8, and then remained stable. To establish the pH effect at acidic conditions on nicosulfuron hydrolysis (experiments in dark), we have run experiments at pH 3.4 and 5 (insert in Fig. 1). Our results are in agreement with the published ones since we found that hydrolysis at pH 3.4 (4%) is higher in comparison to hydrolysis at pH 5 (0.5%) after 30 min of reaction. In addition, results of photolysis at pH 3.4 (9%) and pH 5 (3.5%) after 30 min of reaction, showed that photolysis is more pronounced than hydrolysis.

Fastest photodegradation was achieved at $\text{pH} = 5.0$, i.e. the pure nicosulfuron solution in deionized water (see also Table S2, Supplementary material). The obtained result are similar to the results of Fenoll et al. [16] for the sulfonylureas, including nicosulfuron, where the fastest degradation rate occurred at pH 6–7 near the TiO_2 point of zero charge (PZC). The PZC of TiO_2 depends on the way it is produced, but the usual value in literature for PZC is 6.3 [16]. According to the findings of Pelentridou et al. [27], a possible explanation could be that at low and high pH values, nicosulfuron has chargeable chemical groups ($\text{pK}_a = 4.6$, [3] and there is a repulsion between nicosulfuron and the TiO_2 surface.

It will be shown later (see 3.4.) that the degradation by holes and surface OH radicals is less important than mechanism for nicosulfuron via OH radicals in solution, except in the initial part of the reaction. Although the adsorption is relatively small (less than 5%) it seems that this is enough to influence the pH profile of the reaction.

3.2. Effect of inorganic anions

The salts are commonly present in aqueous media and many researchers found that the inorganic salts from water had a significant effect on photodegradation process of organic compounds [23,24,26,28,29]. To examine the anion effect, we studied the influence of several anions (Cl^- , SO_4^{2-} , NO_3^- and F^-) on the reaction rate. The salt concentration of 20 mM was chosen as before [23] and the pseudo-first order constant values are given in Table S3 (Supplementary material).

3.2.1. Effect of chloride

The reaction inhibition, observed in Fig. 4, when chloride ions are present, can be explained by the competitive adsorption of chloride ions or by their hole scavenging properties. The influence of chloride ions is given by Eqs. (6)–(8) [29–31]. The formed chlorine radicals are transformed further immediately.



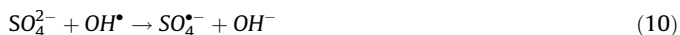
Chloride radicals can react with electrons and thus reduced to anions [32]. Chloride anions are not oxidisable and act as effective inhibitors during degradation [31]. Fig. S2 (Supplementary material) donates the influence of two different concentrations of NaCl (20 and 200 mM). It can be observed that the higher concentration of chloride ions inhibit reaction stronger as a result of more intensive adsorption and reactions with holes and electrons [33].

Fig. 3. The influence of pH on the photocatalytic degradation of nicosulfuron (20 mg L^{-1}) in the presence of TiO_2 (2 g L^{-1}). Symbols present different pH values of the solutions: (■) 3.4; (□) 5.0; (○) 6.4; and (◇) 10.9. The insert shows influence of pH on the degradation rate of nicosulfuron.

Fig. 4. Effect of different anions on the photocatalytic degradation of nicosulfuron (20 mg L^{-1}), at $\text{pH} = 5.0$, in the presence of TiO_2 (2 g L^{-1}). Symbols represent: (■) without salt; (□) NaCl; (○) Na_2SO_4 ; (◇) NaNO_3 ; and (△) NaF. Salt concentration 20 mM.

3.2.2. Effect of sulphate

As far as sulphate anions are concerned, they also influence the reaction by a competitive adsorption, just like chloride anions (Fig. 4). Eqs. (9) and (10) describe the reaction of sulphate anions with positive holes and hydroxyl radicals [28,29]. The reaction inhibition is a result of formed $\text{SO}_4^{\bullet-}$ which is less reactive than $\bullet\text{OH}$ and $h\nu_{\text{B}}^+$ due to the resonance and larger size [34]. $\text{SO}_4^{\bullet-}$ can also react with electron to give sulphate anion (Eq. (11)).



The photocatalytic reaction in the presence of sulphate anions is slower than in the presence of chlorides. In one hand, the adsorption of sulphate anions is greater than chloride since they are larger and two valence anions which will increase adsorption competition [35].

3.2.3. Effect of nitrate

It was reported that at very low concentration (below 0.1 mM) nitrate anions can enhance the reaction rate of photocatalytic degradation of pollutants [36] as a result of the photolysis of nitrate anions. At higher concentrations, as in this work (Fig. 4), the reaction rate inhibition was observed [36,37]. In the excess of nitrate anions a competitive adsorption can occur and decrease the reaction rate. The inhibition is much higher in comparison to chloride anions due to the larger size of anions which leads to a more affective block of catalyst surface [37].

Nitrate anions can also react with positive holes and hydroxyl radical and act as h^+ and radical scavengers (Eqs. (14) and (15) [38].



3.2.4. Effect of fluoride

Fluoride anions are characterized by strong adsorption on the photocatalyst surface of TiO_2 . Also, fluoride anions are stable on oxidation by holes since the redox potential is about 3.6 V for the pair F/F^- [39,40]. So, fluoride can completely cover the catalyst surface and thus inhibit surface OH radical production. This means that when fluoride is present in the system, the degradation is mainly by OH radicals present in the solution. In the absence of fluoride, the surface is hydroxylated and holes and surface OH radicals participate in degradation. As can be seen from Fig. 4, there is a big difference between the reaction rate in the absence and presence of fluoride anions which implies that holes and surface OH radicals also participate in the photocatalytic degradation of nicosulfuron.

3.3. Effect of inorganic cations

Cations of different metals can be found in natural as well as in waste waters. It was suggested that some of these metal ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) should not influence the photodegradation reaction since they are in stable oxidation state [36]. Here, the degradation of nicosulfuron was studied in the presence of different cations of sulphate salts (Na_2SO_4 , CaSO_4 and $\text{Al}_2(\text{SO}_4)_3$). The obtained results are given in Fig. 5 and in Table S4 (Supplementary material). As shown in Fig. 5, all the three salts

Fig. 5. Effect of different cations on the photocatalytic degradation of nicosulfuron (20 mg L^{-1}), at pH = 5.0, in the presence of TiO_2 (2 g L^{-1}). Symbols represent: (■) without salt; (○) Na_2SO_4 ; (□) CaSO_4 ; and (△) $\text{Al}_2(\text{SO}_4)_3$. Salt concentration 20 mM. Insert: pH change during photocatalytic degradation of nicosulfuron in the presence of TiO_2 and $\text{Al}_2(\text{SO}_4)_3$.

exhibit inhibition effect on nicosulfuron photocatalytic degradation.

The inhibition effect of the used salts can be attributed firstly to sulphate ions present in solution. It was pointed out that sulphate anions can influence the reaction by a competitive adsorption, or by the reaction with positive holes and hydroxyl radicals.

The strong inhibition of photocatalytic degradation of nicosulfuron in the presence of aluminium ions can be attributed in one hand to increased concentration of sulphate anions ($\text{Al}_2(\text{SO}_4)_3$) and in other hand to the Al^{3+} adsorption. It was shown that Al^{3+} adsorption occurs when pH value is below the catalyst PZC, although TiO_2 surface and Al^{3+} are charged positive [33]. This is possible, since isolated hydroxyl groups present at catalyst surface are basic and adsorb Al^{3+} . These groups are photoactive, but after adsorption of Al^{3+} the photocatalytic degradation is hindered. Insert in Fig. 5 shows the pH change during the reaction in the presence of Al^{3+} .

Sodium and calcium ions have similar effect on the photodegradation rate but the slightly faster reaction was in the presence of sodium ions.

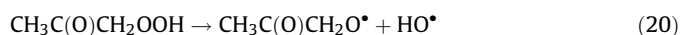
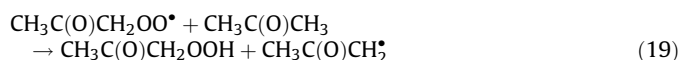
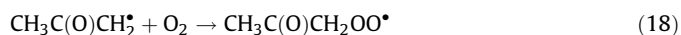
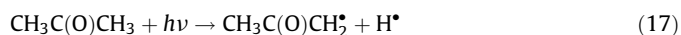
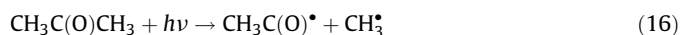
3.4. Effect of isopropanol

isopropanol (2-propanol) as well as methanol or *tert*-butanol are good hydroxyl radical scavenger and are usually used to differentiate between direct oxidation with positive holes and the degradation with $\bullet\text{OH}$ radicals in solution [39–42]. Since adsorption of alcohols on the catalyst surface is relatively small, the oxidation by generated holes in the photocatalytic reaction can be neglected. In this work, different concentrations of isopropanol (0.1, 0.3, 0.5 and 20 mM) were used to estimate the effect on the photocatalytic degradation of nicosulfuron (Fig. 6 and Table S5 (Supplementary material)). Addition of a small amount of isopropanol (0.1 mM) significantly slows the degradation of nicosulfuron. Increase in isopropanol concentration additionally inhibits the reaction. This indicates that $\bullet\text{OH}$ radicals in solution play an important role in the photodegradation of nicosulfuron. Higher concentration of alcohol (20 mM) does not contribute to the additional inhibition of the reaction.

To get better insight in the mechanism of nicosulfuron degradation, reactions in the presence of sodium fluoride and

3.5. Effect of acetone

It has been reported that acetone can act as a photosensitizer or inhibitor [43,44] in photocatalytic reactions, especially photolysis. The behaviour of acetone as photosensitizer, can be described by the following Equations (Eqs. (16)–(20)) [43]:



As a result of these reactions $\cdot\text{OH}$ radicals are formed and may accelerate the reaction. On the other hand, acetone degrades and competes with the pollutant, inhibiting the reaction. In this work, an influence of acetone on photocatalytic degradation of nicosulfuron was studied by varying the concentration of the added acetone in the range 0.1–1 mM. As can be seen from Fig. 8 and Table S6 (Supplementary material), there is an inhibition of the reaction when small amount of acetone was added (0.1 mM). As the concentration of acetone increases, the reaction rate increases. When concentration of acetone was 1 mM, the reaction rate was the same as in the absence of acetone. It seems that the small amount of acetone inhibit the degradation of nicosulfuron by competition while as the concentration increases the amount of $\cdot\text{OH}$ radicals increases and enhance the reaction rate.

3.6. Effect of hydrogen peroxide

The addition of electron acceptors like H_2O_2 can prevent electron-hole recombination. The recombination is undesired (energy waste). Electron acceptors can enhance the photocatalytic reaction rate of pollutant degradation. They can accept the

Fig. 6. The influence of isopropanol on the photocatalytic degradation of nicosulfuron (20 mg L^{-1}) in the presence of TiO_2 (2 g L^{-1}). Symbols represent: (■) 0 mM; (□) 0.1 mM; (△) 0.3 mM; (◇) 0.5 mM and (○) 20 mM of isopropanol.

Fig. 7. The influence of NaF and isopropanol on the photocatalytic degradation of nicosulfuron (20 mg L^{-1}) in the presence of TiO_2 (2 g L^{-1}). Symbols represent: (■) without additives; (□) 20 mM of NaF; (△) 20 mM of isopropanol; (◇) 20 mM of NaF and 20 mM of isopropanol.

isopropanol were compared. As can be seen from Fig. 7, at the same concentration of sodium fluoride and isopropanol, the stronger inhibition was observed with isopropanol. This means that the degradation proceeds mainly by OH radicals in solution. The reaction rate constant in the presence of isopropanol is 16.66 times smaller than in its absence in comparison to the reaction with NaF which is 3.11 times slower than in the absence of NaF (the reaction constants were 0.1667 and 0.0311 min^{-1} for NaF and isopropanol, respectively). The similar effect of alcohol in degradation of herbicide quinmerac was observed by Despotovic et al. [41]. Degradation by holes and surface OH radicals is less important, except in the initial part of the reaction. As the reaction goes on, $\cdot\text{OH}$ radicals in solution become more important. In addition, an experiment with the addition of NaF and isopropanol was performed (Fig. 7). A complete inhibition of photocatalytic reaction was observed. Only the photolysis was present (see Fig. 1).

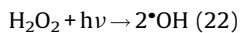
Fig. 8. Effect of different acetone concentrations on the photocatalytic degradation of nicosulfuron (20 mg L^{-1}), at $\text{pH} = 5.0$, in the presence of TiO_2 (2 g L^{-1}). Symbols represent: (■) without acetone; (□) 1 mM; (△) 0.5 mM; (◇) 0.3 mM; and (○) 0.1 mM.

conduction band electrons or increase the concentration of OH or other radicals [29,36,39,45,46]).

The reaction with conduction band electrons can be described by Eq. (21):



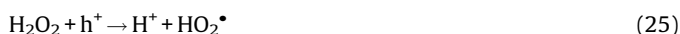
While the generation of radicals can be described by Eq. (22):



On the other hand, H_2O_2 can scavenge the $\bullet\text{OH}$ radicals present in the system, as well as the valence band holes. The $\bullet\text{OH}$ radicals can be formed from H_2O_2 (photolysis, Eq. (22)) or from the reaction of OH^- and holes (Eq. (23)).



The reaction of H_2O_2 with $\bullet\text{OH}$ radicals or the holes leads to the formation of free $\text{HO}_2\bullet$, which is a weaker oxidant in comparison to $\bullet\text{OH}$ radical (Eqs. (24) and (25)): In addition, $\text{HO}_2\bullet$ react with $\bullet\text{OH}$ radicals (Eq. (26)) to form water and oxygen.



In addition, $\text{HO}_2\bullet$ react with $\bullet\text{OH}$ radicals (Eq. (26)) to form water and oxygen.



Higher concentration of H_2O_2 can influence the amount of UV light needed for the photocatalytic reaction by its absorption [45]. Also, H_2O_2 can modify the TiO_2 surface when adsorbed and reduce its catalytic activity [47].

The concentration of added H_2O_2 was varied from 0 to 10 mM and the results are presented in Fig. 9 and Table S7 (Supplementary material). Even at low concentration of H_2O_2 (0.1 mM) a decrease of the reaction rate was observed while at higher concentrations of H_2O_2 one can see clear inhibition of the reaction. This means that H_2O_2 is rather an inhibitor than an accelerator of the photocatalytic degradation of nicosulfuron.

Fig. 9. The influence of hydrogen peroxide on the photocatalytic degradation of nicosulfuron (20 mg L^{-1}) in the presence of TiO_2 (2 g L^{-1}). Symbols represent different hydrogen peroxide concentrations in the solution: (■) without hydrogen peroxide; (○) 0.1 mM; (□) 0.25 mM; (△) 2.5 mM; (◇) 5.0 mM and (◇) 10 mM.

Fig. 10. Time dependence of nicosulfuron, TOC and inorganic ions (nitrate and ammonium) concentration during the photocatalytic degradation of nicosulfuron (20 mg L^{-1}), at pH = 5.0, in the presence of TiO_2 (2 g L^{-1}): (○) NH_4^+ ; (□) NO_3^- ; (■) TOC; (◇) $C_{\text{nicosulfuron}}$.

3.7. Mineralization study of nicosulfuron

According to the obtained results of nicosulfuron photocatalytic degradation based on a HPLC analysis, 100% of 20 mg L^{-1} of nicosulfuron was degraded during 30 min of irradiation. On the other hand, when the mineralization of nicosulfuron was studied by the total organic carbon analysis, for 90 min, the TOC elimination was 69% (Fig. 10). This indicates that the TOC removal rate was not proportional to the rate of nicosulfuron degradation. An ion chromatography analysis was also performed (Fig. 10), having in mind the molecular structure of nicosulfuron, one could expect, as a result of nicosulfuron degradation, the formation of sulphate, ammonium and nitrate ions. Our results (Fig. 10) show the formation of ammonium and nitrate ions only. The concentration of sulphate ions was under the detection limit, which is in contrast to the results reported in previous studies concerning other sulfonylureas [10,48]. This indicates that the sulfur is still present in the products of photodegradation (31% of organic carbon remains in the solution).

The concentration of NO_3^- and NH_4^+ ions after 90 min of illumination of the nicosulfuron solution were 2.90 mg L^{-1} and 1.61 mg L^{-1} , respectively. A nicosulfuron molecule has six nitrogen atoms and if there is 100% mineralization it is possible to obtain (theoretically) 5.26 mg L^{-1} of NH_4^+ (if all nitrogen is converted to NH_4^+) or 18.11 mg L^{-1} of NO_3^- (if all nitrogen is converted to NO_3^-) during the oxidation of nicosulfuron (20 mg L^{-1}). According to the literature data [25], the amount of NH_4^+ and NO_3^- ions depends on the $\text{NH}_4^+/\text{NO}_3^-$ ratio. As it can be seen from Fig. 10, ammonium and nitrate ions are quickly released and after 90 min of irradiation they reach about 46% of the stoichiometric nitrogen content (about 16 % of originated nitrogen converted to NO_3^- and about 30 % of originated nitrogen converted to NH_4^+).

3.8. Identification of photodegradation products

two studies can be found in literature where detailed nicosulfuron degradation was investigated by photolysis. Benzi et al. [2] have recorded five, while ter Halle et al. [14] have found six photodegradation products. Among those products, only one was formed by the opening of the pyrimidine ring.

In order to identify degradation products under photocatalytic conditions, aqueous nicosulfuron solutions used for the degradation study were submitted to HPLC–MSⁿ analysis. Full mass spectra

in positive and negative ionization mode were recorded for samples with irradiation time ranging from 0 to 90 min (Table S8 and Figs. S3 and S4 (Supplementary material)). The most intense m/z signals were extracted and further fragmented in order to obtain MS/MS fragments. The highest number of degradation products could be found in the sample after 5 min of irradiation. Total of 6 intense m/z signals in PI, and 7 intense m/z signals in NI could be observed. But in the sample with irradiation time of 10 min only four intense m/z signals remain. Observed m/z signals produced signals in PI and NI mode (Table S8, Supplementary material). These degradation products are present also in the 20 min sample but with reduced intensities. In the samples with higher irradiation time degradation products could not be detected (Fig. S4, Supplementary material). The 10 min sample was analysed by direct infusion in order to obtain MSⁿ fragments of the most intense m/z values. The most intense m/z signals found in the samples with irradiation time ranging from 5 to 20 min with their MSⁿ fragments are listed in Table S8 (Supplementary material).

HPLC–MS chromatograms extracted from the total ion chromatogram for five intermediate photodegradation products recorded in this study are presented in Fig. S3b–f (Supplementary material). Fig. S3a presents HPLC–MS chromatogram of starting nicosulfuron. The retention time of nicosulfuron was 9.35 min. Nicosulfuron gave signals in both ionization modes with similar intensities. In PI protonated molecular ion at m/z 411 [M+H]⁺ along with sodium, m/z 433 [M+Na]⁺, and potassium, m/z 449 [M+K]⁺, adducts could be found. In NI, nicosulfuron forms deprotonated molecular ion ([M–H][–]) at m/z 409.

The M1 intermediate product corresponds to a compound with molecular weight (Mw) 314. It could be detected in both modes, corresponding to m/z 315 and 313, respectively. This transformation product can be detected after five minutes of irradiation, with the highest intensity. With increased irradiation, the time intensity of M1 declines, and in the samples exposed to irradiation for more than 20 min, it can not be detected. This structure is formed by the opening of the pyrimidine ring and the retention of the pyridine ring. This photodegradation product is in accordance with the study of Benzi et al. [2].

Other detected photodegradation products (except M3) have a higher molar mass than M1, indicating that the initial degradation of nicosulfuron was recorded.

The possible intermediate photodegradation product M5 corresponds to a compound with Mw 386. M5 is present in all samples and its intensity varies according to Fig. S4 a,b (Supplementary material), but after 30 min it completely disappears. This structure is formed by the loss of two methyl groups (C–O bond cleavage), opening of the pyrimidine ring and the retention of the pyridine ring.

The M4 intermediate product corresponds to a compound with Mw 372. The intensity of M4 decreases with the increasing irradiation time. This structure is formed by the loss of one methyl group (C–O bond cleavage), and the opening of the pyrimidine ring.

The possible intermediate photodegradation product M2 corresponds to the compound with Mw 328. It is evident from Fig. S4 a,b (Supplementary material) that the intensity of M2 increases with the irradiation time. After 20 min, the intensity of M2 decreases and after 30 min of irradiation this intermediate product disappears. This structure is a result of the opening of the pyrimidine ring (C–N bond cleavage) and the insertion of a methyl group into M1 intermediate product.

The M3 intermediate product corresponds to the compound with Mw 230. This product can be found in MS² fragments of M1 and M4. Here, a loss of the pyrimidine ring and one amide bond is evident. This intermediate product is also in accordance with the study of Benzi et al. [2] and ter Halle et al. [14].

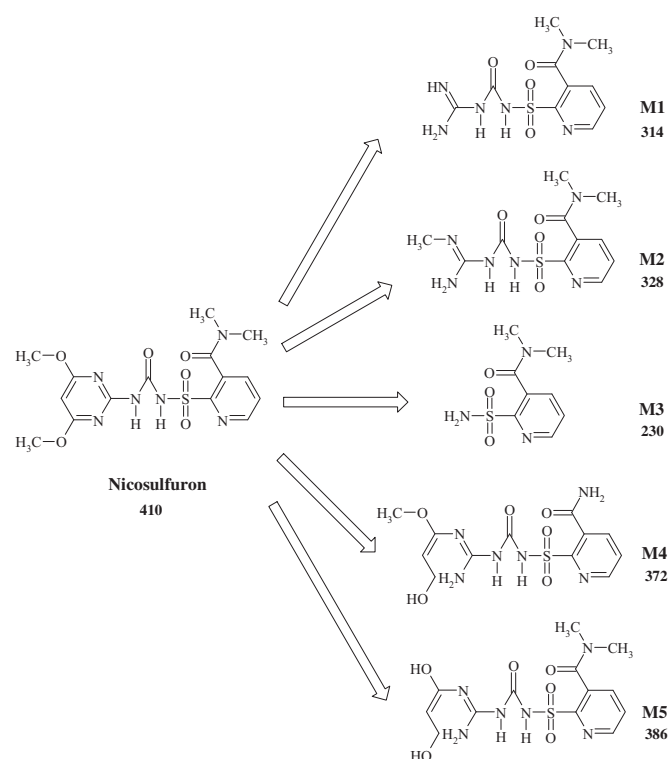


Fig. 11. Proposed structures of the photodegradation products during the photocatalytic degradation of nicosulfuron (20 mg L^{–1}), at pH = 5.0, in the presence of TiO₂ (2 g L^{–1}).

It should be pointed out that M1–M4 intermediate photodegradation products were not detected after 60 min of reaction. The presence of M5 is negligible.

The proposed structures of the obtained photodegradation products are presented in Fig. 11.

These structures indicate that all sulfur is still present in the photodegradation products, which was confirmed by IC (Fig. 10). The formation of the photodegradation product M3 (with 3 nitrogen atoms in molecule) as well as the possible formation of other smaller molecules (with less nitrogen atoms in molecule—not detected) after 60 min of the reaction is the cause of nitrogen loss from nicosulfuron molecule (46%). As can be seen from Fig. 10, the concentrations of NO₃[–] and NH₄⁺ ions increase until the end of the reaction which confirms the loss of molecular nitrogen. In addition, TOC decreases until the end of the reaction. The smaller degradation products found by Benzi et al. [2] and ter Halle et al. [14] were not recorded, but TOC loss (69%) and the final concentration of NO₃[–] and NH₄⁺ ions after 90 min of illumination of the nicosulfuron solution indicates the potential formation of smaller degradation products.

3.9. Phytotoxicity testing using mung bean (*Vigna mungo*) seeds

Nicosulfuron is the herbicide used for weed control in corn field. Great mobility in the soil of nicosulfuron herbicide can easily cause groundwater contamination. Besides, it was observed that nicosulfuron can induce phytotoxic effects in some sensitive corn sorts even in small concentrations [49].

The phytotoxicity of the samples before and after the photocatalytic degradation of nicosulfuron was examined using the mung bean seeds and the obtained results are presented in Fig. 12. It is evident from Fig. 12a that after the degradation reaction, decrease in the phytotoxicity was achieved. Namely, phytotoxicity of 56.8% was calculated in the sample before the degradation,

Fig. 12. a) Phytotoxicity of nicosulfuron before and after the degradation; b) Mung bean seed germination in the sample: 1. after degradation, 2. before degradation, 3. control.

while in the sample after the degradation the phytotoxicity reached the value of 14.8%.

Furthermore, the obtained radicle length in the sample after the degradation of 6.9 cm is a good indicator of toxicity reduction in comparison with radicle length in the sample before degradation of 3.5 cm. Radicle length reduction of ~15% in the sample after the degradation (6.9 cm) compared with radicle length in the control (8.1 cm) indicates that photocatalytic degradation of nicosulfuron using TiO_2 is a sustainable and environmentally friendly method of herbicide degradation.

4. Conclusion

The investigation of the photocatalytic degradation of nicosulfuron in the presence of TiO_2 under UV polychromatic light showed that the optimal concentration of catalyst was 1 g L^{-1} at the concentration of nicosulfuron of 20 mg L^{-1} . On the other hand, the highest reaction rate was obtained by using 2 g L^{-1} of TiO_2 . the pH influence was also studied and it was found that the reaction was faster in acidic than in base media. The presence of salts (cations and anions) inhibited the reaction, the influence of anions on the reaction was $\text{Cl}^- > \text{SO}_4^{2-} > \text{F}^- > \text{NO}_3^-$, while the influence of cations was $\text{Na}^+ > \text{Ca}^{2+} > \text{Al}^{3+}$. due to the small adsorption of nicosulfuron on the catalyst surface, the inhibitory effect of inorganic ions can be attributed rather to the scavenger role of anions than to the competitive adsorption. The addition of isopropanol inhibited the reaction strongly indicating that $\cdot\text{OH}$ radicals in solution play an important role in the photodegradation of nicosulfuron. The reaction was also inhibited by the addition of acetone and hydrogen peroxide. The addition of sodium fluoride and isopropanol completely inhibited the photocatalytic reaction. After 30 min of irradiation, HPLC analysis showed that 100% of nicosulfuron were degraded, while after 90 min the mineralization established by a TOC analysis was 69%. The sulphate ions were not detected in solutions, proving that a sulfur atom was present in the possible photodegradation products, while the concentration of ammonium and nitrate ions reached 46 % of the stoichiometric nitrogen content. Five intermediates, derived from the opening of the pyrimidine ring, were identified using HPLC–MS. Three of these photodegradation products are different than those obtained in previous studies. The highest concentrations of intermediates were observed at the beginning of the reaction and after 60 min their concentrations were negligible, but the formation of smaller molecules is not excluded. The phytotoxicity experiments using mung bean seeds showed that phytotoxicity was reduced from 56.8% before the degradation to 14.8% after 90 min of photocatalysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jphotochem.2016.12.031>.

References

- [1] S. Ahmed, M.G. Rasul, R. Brown, M.A. Hashib, Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review, *J. Environ. Manage.* 92 (2011) 311–330.
- [2] M. Benzi, E. Robotti, V. Gianotti, HPLC–DAD–MSⁿ to investigate the photodegradation pathway of nicosulfuron in aqueous solution, *Anal. Bioanal. Chem.* 399 (2011) 1705–1714.
- [3] C. MacBean, *The Pesticide Manual*, sixteenth ed., BCPC, Alton, Hampshire, UK, 2012.
- [4] European Food Safety Authority, Conclusion regarding the peer review of the pesticide risk assessment of the active substance nicosulfuron, *EFSA J.* 6 (2008) 1–91 (RN-120).
- [5] J. Sabadie, Nicosulfuron: alcoholysis, chemical hydrolysis, and degradation on various minerals, *J. Agric. Food Chem.* 50 (2002) 526–531.
- [6] A.K. Sarmah, J. Sabadie, Hydrolysis of sulfonylurea herbicides in soils and aqueous solutions: a review, *J. Agr. Food Chem.* 50 (2002) 6253–6265.
- [7] H. Zhang, W. Mu, Z. Hou, X. Wu, W. Zhao, X. Zhang, H. Pan, S. Zhang, Biodegradation of nicosulfuron by the bacterium *Serratia marcescens* N80, *J. Environ. Sci. Health B* 47 (2012) 153–160.
- [8] E. Vuillet, C. Emmelin, J.M. Chovelon, C. Guillard, J.M. Herrmann, Photocatalytic degradation of sulfonylurea herbicides in aqueous TiO_2 , *Appl. Catal. B* 38 (2002) 127–137.
- [9] E. Vuillet, C. Emmelin, M.F. Grenier-Loustallot, O. Paissé, J.M. Chovelon, Simulated sunlight-induced photodegradations of triasulfuron and cinosulfuron in aqueous solutions, *J. Agric. Food Chem.* 50 (2002) 1081–1088.
- [10] E. Vuillet, C. Emmelin, J.M. Chovelon, C. Guillard, J.M. Herrmann, Photocatalytic degradation of the herbicide cinosulfuron in aqueous TiO_2 suspension, *Environ. Chem. Lett.* 1 (2003) 62–67.
- [11] E. Vuillet, C. Emmelin, J.M. Chovelon, Influence of pH and irradiation wavelength on the photochemical degradation of sulfonylureas, *J. Photochem. Photobiol. A* 163 (2004) 69–75.
- [12] V. Maurino, C. Minero, E. Pelizzetti, M. Vincenti, Photocatalytic transformation of sulfonylurea herbicides over irradiated titanium dioxide particle, *Colloid Surf. A* 151 (1999) 329–338.
- [13] M. Benzi, E. Robotti, V. Gianotti, Study on the photodegradation of amidosulfuron in aqueous solutions by LC–MS/MS, *Environ. Sci. Pollut. Res.* 20 (2013) 9034–9043.
- [14] A. ter Halle, D. Lavieille, C. Richard, The effect of mixing two herbicides mesotrione and nicosulfuron on their photochemical reactivity on cuticular wax film, *Chemosphere* 79 (2010) 482–487.
- [15] J. Fenoll, P. Hellín, P. Flores, C.M. Martínez, S. Navarro, Photocatalytic degradation of five sulfonylurea herbicides in aqueous semiconductor suspensions under natural sunlight, *Chemosphere* 87 (2012) 954–961.
- [16] J. Fenoll, P. Sabater, G. Navarro, N. Vela, G.W. Perez-Lucas, S. Navarro, Abatement kinetics of 30 sulfonylurea herbicide residues in water by photocatalytic treatment with semiconductor materials, *J. Environ. Manage.* 130 (2013) 361–368.

- [17] Z.S. Banu, K. Murugesan, Phytotoxicity analysis of textile effluent and relative germination study on dicot seeds, *International Journal of Research in Chemistry and Environment* 3 (2013) 155–162.
- [18] F. Han, V.S.R. Kambala, M. Srinivasan, D. Rajarathnam, R. Naidu, Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: a review, *Appl. Catal. A* 359 (2009) 25–40.
- [19] K.H. Wang, Y.H. Hsieh, M.Y. Chou, C. Chang, Photocatalytic degradation of 2-chloro and 2-nitrophenol by titanium dioxide suspensions in aqueous solution, *Appl. Catal. B* 21 (1999) 1–8.
- [20] P. Fernández-Ibanez, S. Malato, F.J. de las Nieves, Relationship between TiO₂ particle size and reactor diameter in solar photoreactors efficiency, *Catal. Today* 54 (1999) 195–204.
- [21] D. Robert, B. Dongui, J.V. Weber, Heterogeneous photocatalytic degradation of 3-nitroacetophenone in TiO₂ aqueous suspension, *J. Photochem. Photobiol. A* 156 (2003) 195–200.
- [22] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO₂, *Sol. Energy Mater. Sol. Cells* 77 (2003) 65–82.
- [23] D. Mijin, M. Savić, P. Snežana, A. Smiljanić, O. Glavaški, M. Jovanović, S. Petrović, A study of the photocatalytic degradation of metatriton in ZnO water suspensions, *Desalination* 249 (2009) 286–292.
- [24] A. Tomašević, D. Mijin, E. Kiss, Photochemical behavior of the insecticide methomyl under different conditions, *Sep. Sci. Technol.* 45 (2010) 1617–1627.
- [25] A. Tomašević, E. Kiss, S. Petrović, D. Mijin, Study on the photocatalytic degradation of insecticide methomyl in water, *Desalination* 262 (2010) 228–234.
- [26] A. Tomašević, D. Mijin, S. Gašić, E. Kiss, The influence of polychromatic light on methomyl degradation in TiO₂ and ZnO aqueous suspension, *Desalin. Water Treat.* 52 (2014) 4342–4349.
- [27] K. Pelentridou, E. Stathatos, H. Karasali, D.D. Dionysiou, P. Lianos, Photocatalytic degradation of a water soluble herbicide by pure and noble metal deposited TiO₂ nanocrystalline films, *Inter. J. Photoenergy* (2008) (art. no. 978329).
- [28] C. Hu, J.C. Yu, Z. Hao, P.K. Wong, Effects of acidity and inorganic ions on the photocatalytic degradation of different azo dyes, *Appl. Catal. B* 46 (2003) 35–47.
- [29] Y. Wang, K. Lu, C. Feng, Influence of inorganic anions and organic additives on photocatalytic degradation of methyl orange with supported polyoxometalates as photocatalyst, *J. Rare Earths* 31 (2013) 360–365.
- [30] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar light induced and TiO₂ assisted degradation of textile dye reactive blue 4, *Chemosphere* 46 (2002) 1173–1181.
- [31] H.Y. Chen, O. Zahraa, M. Bouchy, Inhibition of the adsorption and photocatalytic degradation of an organic contaminant in an aqueous suspension of TiO₂ by inorganic ions, *J. Photochem. Photobiol. A Chem.* 108 (1997) 37–44.
- [32] A. Lair, C. Ferronato, J.-M. Chovelon, J.-M. Herrmann, Naphthalene degradation in water by heterogeneous photocatalysis: an investigation of the influence of inorganic anions, *J. Photochem. Photobiol. A Chem.* 193 (2008) 193–203.
- [33] D. Santiago, J. Arana, O. Gonzalez-Díaz, M.E. Aleman-Dominguez, C. Acosta-Dacal Andrea, C. Fernandez-Rodriguez, J. Perez-Pena, J.M. Dona-Rodriguez, Effect of inorganic ions on the photocatalytic treatment of agro-industrial wastewaters containing imazalil, *Appl. Catal. B* 156–157 (2014) 284–292.
- [34] R.A. Burns, J.C. Crittenden, D.W. Hand, V.H. Selzer, L.L. Sutter, S.R. Salman, Effect of inorganic ions in heterogeneous photocatalysis of TCE, *J. Environ. Eng.* 125 (1999) 77.
- [35] Y. Xiaojun, B. Ruiling, Y. Shuili, Effect of inorganic ions on the photocatalytic degradation of humic acid, *Russ. J. Phys. Chem. A* 86 (2012) 1318–1325.
- [36] C. Wang, L. Zhu, M. Wei, P. Chen, G. Shan, Photolytic reaction mechanism and impacts of coexisting substances on photodegradation of bisphenol A by Bi₂WO₆ in water, *Water Res.* 46 (2012) 845–853.
- [37] M.-H. Chen, C.-C. Chen, R.-J. Wu, C.-S. Lu, Heterogeneous photocatalytic degradation of disulfoton in aqueous TiO₂ suspensions: parameter and reaction pathway investigations, *J. Chin. Chem. Soc.* 60 (2013) 380–390.
- [38] B. Chládková, E. Evgenidou, L. Kvítek, A. Panáček, R. Zboril, P. Kovář, D. Lambropoulou, Adsorption and photocatalysis of nanocrystalline TiO₂ particles for Reactive Red 195 removal: effect of humic acids, anions and scavengers, *Environ. Sci. Pollut. Res.* 22 (2015) 16514–16524.
- [39] B. Abramovic, V. Despotovic, D. Sojic, N. Fincur, Mechanism of clomazone photocatalytic degradation: hydroxyl radical, electron and hole scavengers, *Reac. Kinet. Mech. Cat.* 115 (2015) 67–79.
- [40] Y. Chen, S. Yang, K. Wang, L. Lou, Role of primary active species and TiO₂ surface characteristic in UV-illuminated photodegradation of Acid Orange 7, *J. Photochem. Photobiol. A Chem.* 172 (2005) 47–54.
- [41] V.N. Despotović, B.F. Abramović, D.V. Šojić, S.J. Kler, M.B. Dalmacija, L.J. Bjelica, D.Z. Orčić, Photocatalytic degradation of herbicide quinnex in various types of natural water, *Water Air. Soil Pollut.* 223 (2012) 3009–3020.
- [42] W.-L. Wang, Q.-Y. Wu, Z.-M. Wang, H.-Y. Hu, N. Negishi, M. Torimura, Photocatalytic degradation of the antiviral drug tamiflu by UV-A/TiO₂: Kinetics and mechanisms, *Chemosphere* 138 (2015) 988–994.
- [43] X. Sun, G. Yang, X. Cao, Z. Lin, Photochemical degradation of triadimefon in seawater, *J. Ocean Univ. Chin.* 7 (2008) 171–176.
- [44] X. Li, J. Huang, L. Fang, G. Yu, H. Lin, L. Wang, Photodegradation of 2,2',4,4'-tetrabromodiphenyl ether in nonionic surfactant solutions, *Chemosphere* 78 (2008) 752–759.
- [45] L. Wei, C. Shifu, Z. Wei, Z. Sujuan, Titanium dioxide mediated photocatalytic degradation of methamidophos in aqueous phase, *J. Hazard. Mater.* 164 (2009) 154–160.
- [46] O.S. Glavaški, S.D. Petrović, V.N. Rajaković-Ognjanović, T.M. Zeremski, A.M. Dugandžić, D.Ž. Mijin, Photodegradation of dimethenamid-P in deionised and ground water, *Chem. Ind. Chem. Eng. Q.* 22 (2016) 101–110.
- [47] U.G. Akpan, B.H. Hameed, Parameters affecting the photocatalytic degradation of dyes using TiO₂-based photocatalysts: a review, *J. Hazard. Mater.* 170 (2009) 520–529.
- [48] M. Sleiman, P. Conchon, C. Ferronato, J.M. Chovelon, Iodosulfuron degradation by TiO₂ photocatalysis: kinetic and reactional pathway investigations, *Appl. Catal. B* 71 (2007) 279–290.
- [49] X.H. Lu, Z.H. Kang, Y.N. Wang, J.G. Dong, J.L. Zhang, Degradation of nicosulfuron by *Bacillus subtilis* YB1 and *Aspergillus niger* YF1, *Appl. Biochem. Micro.* 48 (2012) 460–466.