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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 $TiO_2$ 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 ($Cl^-$, $SO_4^{2-}$, $NO_3^-$ and $F^-$) and cations ($Na^+$, $Ca^{2+}$, $Al^{3+}$) 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 $^{\bullet}OH$ 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.


## 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 derivates, 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-ylcarbamoylsulfamoyl)-*N*,*N*-dimethylnicotinamide ($C_{15}H_{18}N_6O_6S$), 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 meristemic 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 biodegradated 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 $TiO_2$ photocatalytic degradation and photolysis of cinosulfuron and triasulfuron; Maurino et al. [12] studied $TiO_2$ 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 withought $Na_2S_2O_8$), $WO_3$, $SnO_2$ 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 $Na_2S_2O_8$ [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 μm 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 $Al_2(SO_4)_3$ was investigated, $Al_2(SO_4)_3$ 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 μm 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 mm × 4.6 mm i.d., 5 μm 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 μl ($t_R$(nicosulfuron) = 3.0 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 ($NaCO_3$/$NaHCO_3$); flow rate 1 ml $min^{-1}$ corresponding to the retention times: $t_R(NO_2^-)$ = 6.1 min; $t_R(NO_3^-)$ = 8.3 min; $t_R(SO_4^{2-})$ = 14.5 min; $t_R(NH_4^+)$ = 8.9 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 × 4.6 mm i.d. and 3.5 μm particle size (Agilent Technologies, Santa Clara, CA, USA) was used for the separation of the analytes. A pre-column was also installed, 12.5 × 4.6 mm i.d. and 5 μm 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 μL 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]:

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

#### 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