

UNIVERSITY OF BELGRADE  
TECHNICAL FACULTY BOR

# PROCEEDINGS

OF THE 25<sup>th</sup> INTERNATIONAL CONFERENCE ON  
ECOLOGICAL TRUTH

XXV

YEARS

*EcoIst '17*

**Editors**

**Radoje V. Pantovic**

**Zoran S. Marković**

Vrnjacka Banja, Serbia  
12-15 June 2017

UNIVERSITY OF BELGRADE  
TECHNICAL FACULTY BOR



XXV International Conference  
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Edited by  
**Radoje V. PANTOVIC**  
and  
**Zoran S. MARKOVIC**

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## DEGRADATION OF HERBICIDES WITH CHLORINE DIOXIDE: DEGRADATION EFFICIENCY AND TOXICITY TEST

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### ABSTRACT

The main objective of this study was to find optimal parameters for degradation of herbicides, such as nicosulfuron and thifensulfuron-methyl, with chlorine dioxide in deionized water. In order to examine the optimal parameters, degradation of herbicides was investigated under light or dark conditions with different amount of chlorine dioxide (5 and 10 ppm), different time of degradation (30 min, 1, 2, 3, 6 and 24 h) and at different pH values (3, 7 and 9). Degradation efficiency of herbicides was monitored using HPLC-DAD. Acute toxicity tests were performed for degradation products after the treatment with chlorine dioxide.

**Key words:** herbicides, chlorine dioxide, HPLC, degradation efficiency, toxicological analysis.

### INTRODUCTION

Pesticides are very hazardous pollutants that can persist in the aquatic environment for many years [1]. Contamination of soil and ground water by pesticides applied to soil and swept by transport processes such as leaching or runoff is posing an increasingly serious environmental problem. Besides that, herbicides are one of the most used groups of organic compounds, especially for treatments in agro- and horticulture [2]. They are used for weed control in crops. The weed reduces the yield, increases the cost of agricultural production and can reduce crop quality [3]. The widespread use of herbicides and pesticides are in general in agricultural and non-agricultural purposes, and has resulted in the presence of their residues in the various environmental matrices [4]. The land becomes contaminated from the use of herbicides, which are well soluble in water. They, as well as their degradation products, are washed away and get into ground waters, thereby contaminating them [5, 6].

Nicosulfuron, chemically defined as 2-[(4,6-dimethoxypyrimidin-2-yl)carbamoylsulfamoyl]-N,N-dimethylpyridine-3-carboxamide (NS; Figure 1), and thifensulfuron-methyl, chemically defined as methyl 3-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)carbamoylsulfamoyl]thiophene-2-carboxylate (TFSM; Figure 1) are

sulfonylurea herbicides typically used to control weeds in post-emergence treatments. Several authors have studied different properties of nicosulfuron pesticide such as its degradation or its effect in the grown of different vegetables. Adsorption and desorption of nicosulfuron in soils [7, 8] and clay minerals [9] have been studied.

Accordingly, in order to reduce the harmfulness of pesticide residues, different treatments are used for their degradation and removal. One way is by using chlorine dioxide ( $\text{ClO}_2$ ) [10]. Chlorine dioxide is a very powerful means for the disinfection and highly selective oxidizing agent ( $E_0 = 0.936 \text{ V}$ ), so that it can selectively oxidize specific functional groups such as phenolic groups, and tertiary amines [11, 12]. It achieves a very high solubility in water, especially cold. Chlorine dioxide decomposes under the influence of UV rays, high temperature and  $\text{pH} > 12$ . It should not be stored for a long time because it slowly dimerizes to chlorine and oxygen. It is suitable for the treatment of apples, lettuce and the minced meat in order to reduce the microbial activity, for the degradation of certain drugs, as well as for the removal of pesticides on fresh fruits and vegetables [13, 14]. In literature there were data for removal of isoproturon, ametryn, methiocarb, phorate, diazinon and phenylurea pesticides [15, 16, 17, 18]. Chlorine dioxide is used as a disinfecting/oxidizing agent in the treatment of drinking water. In comparison with chlorine, it has a stronger antimicrobial activity, and compared with the ozone and chlorine does not give toxic products such as trihalo-methane, halogen acids and ketones. The disadvantage of chlorine dioxide is in the fact that chlorine dioxide is transformed into chlorite and chlorate anion during treatment (about 70% of chlorine dioxide is transformed in chlorite and 10% in chlorate), which have a negative impact on human health, because they lead to changes in the red blood cells.

Chlorine dioxide was efficiently used for degradation of sulfonylurea herbicides: thifensulfuron-methyl and nicosulfuron. This is the first study of degradation of these herbicides with chlorine dioxide. The objectives of this study were to: a) investigate and optimize degradation of sulfonylurea herbicides: thifensulfuron-methyl and nicosulfuron, with chlorine dioxide in deionized water, b) investigate degradation efficiency of herbicides using HPLC-DAD, and c) examine toxicity of degradation product of herbicides after chlorine dioxide treatment.

## **MATERIALS AND METHODS**

Nicosulfuron and thifensulfuron-methyl (technical grade, 98%) were both supplied from Institute for Plant Protection, Belgrade. The pure stock solution of chlorine dioxide ( $3 \text{ g L}^{-1}$ ) was prepared by mixing sodium chlorite (Superior Water Disinfection Power, TwinOxide®) and sodium bisulphate (Superior Water Disinfection Power, TwinOxide®), in 1 L of distilled water. The exact concentration of chlorine dioxide in the stock solution was quantified using 4500- $\text{ClO}_2$  DPD method according to the Standard Method [19]. Sodium-thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ , p.a., Merck) was used as received.

Acetonitrile (> 99.9%, Sigma-Aldrich HPLC grade), formic acid (Fluka analytical HPLC grade,) and water (HPLC grade water, Sigma-Aldrich) were used for HPLC analysis. Syringe filters (25 mm, PTFE membrane  $0.45 \mu\text{m}$ ) were obtained from Agilent Technologies.

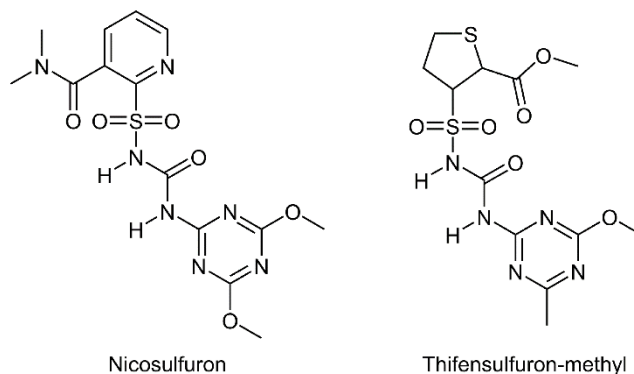
In all experiments concentration of pesticides was 10 ppm. Pesticides were dissolved in acetonitrile and then were diluted using ultra-pure water to the desired concentration. Pesticide solutions were treated with a solution of chlorine dioxide (concentrations of 5 and 10 ppm). Samples were taken from reaction mixture after 30 min, 1 h, 2 h, 3 h, 6 h and 24 h of degradation, and the reaction is interrupted by degradation of a standard 0.1 mol dm<sup>-3</sup> solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (in 10 mL of sample was added approximately 0.3 mL of a solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>). In order to optimize the conditions for degradation of pesticides, degradation was investigated in the dark and in the light, as well as at different pH values (3, 7 and 9). The pH values were adjusted with sulfuric acid (conc. 98%, Sigma-Aldrich) and sodium-hydroxide (analytical grade Sigma-Aldrich).

Degradation efficiency of pesticides was monitored using HPLC (Dionex Ultimate 3000, Thermo Fisher) with photodiode array detection on Hypersil Gold aQ C18 analytical column (150 mm x 3 mm, 3 μm) at 40 °C. Mobile phase consisted of 0.1% formic acid water solution as component A and acetonitrile as component B. The chromatographic elution was conducted at flow rate of 0.6 ml/min in gradient mode: 5 – 95% B in 8 min. Injection volume was 25 μl. Data analysis was performed with software Chromeleon, v6.8 (ThermoFisher Scientific, Bremen, Germany). At appropriate time intervals samples were taken from reaction mixture and quenched using Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Degradation efficiency was calculated for each sample by the equation:

$$\eta = \frac{P_0 - P_t}{P_0} * 100$$

where  $\eta$  was degradation efficiency (%);  $P_0$  was peak area of initial pesticide concentration;  $P_t$  (mAU/min) was peak area of residual pesticide concentration.

Acute toxicity tests with *Daphnia magna* were performed according to standardized guidelines OECD 202 [20] with temperature 21±1 °C and photoperiod of 16 h light/8 h dark. Five *Daphnia magna* neonates not older than 24 h were placed in each vessel with 25 ml of the tested medium (dilution medium was prepared according to the standard method ISO 6341). Acute toxicity tests were performed in borosilicate glasses with control and five test dilutions (6.25%, 12.5%, 25%, 50%, and 100%) with four replicates per dilution. Neonates were not fed during the exposure. Endpoint was the mortality of neonata. Toxic effect for each sample was expressed as the percentage of mortality. Tests were considered valid if the mortality in the control did not exceed 10 %. Immobilization of the neonates was observed after 24 and 48 h, and the results were compared to the control. The LC<sub>50</sub> (lethal concentration which causes mortality of test organism by 50%) values with 95% confidence intervals were estimated by regression model: Spearman–Karber using TesTox software, version 1.0. We have analyzed the degradation products of herbicides after 24 h of treatment of chlorine dioxide.



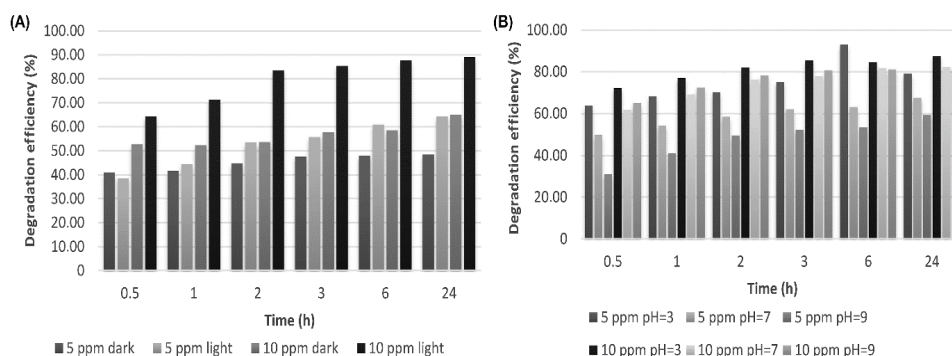
**Figure 1.** Chemical structure of the herbicides

## RESULTS AND DISCUSSION

In view of the increasing usage of chlorine dioxide in water treatment it is important to investigate its reactivity with common organic contaminants, such as pesticides. Optimization of chlorine dioxide dosage, different time of degradation and at different pH values of solutions were performed in system with deionized water. Chlorine dioxide was added in deionized water solution of pesticide. Concentration of pesticide was 10 ppm.

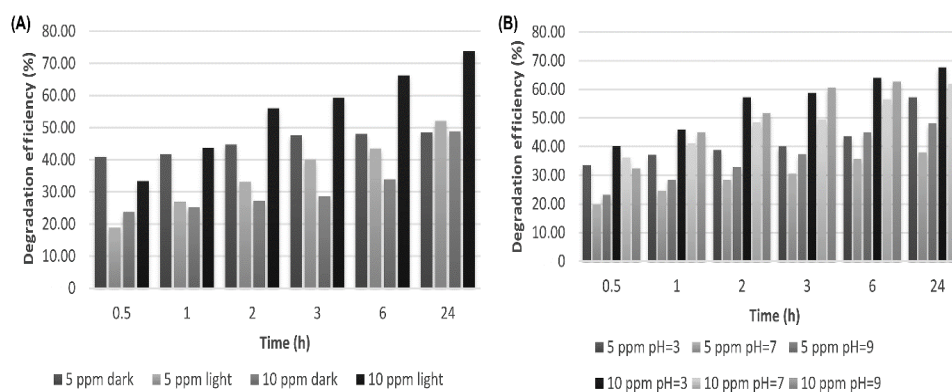
The percentage of degradation was monitored by HPLC analysis on the basis of the pesticide peak area reduction after degradation compared to the peak area of the pesticides prior to degradation.

Analysis of nicosulfuron samples showed that at a concentration of 5 ppm  $\text{ClO}_2$ , high efficiency of degradation was not achieved in the dark or in the light (in the dark, after 24 h, 48.47%; in the light, after 24 h, 64.27%) (Figure 2. A), whereas at a concentration of 10 ppm  $\text{ClO}_2$  good efficiency of degradation also wasn't achieved in the dark (64.92% after 24 h). However good degradation efficiency was achieved in the light (after 24 h, 89.03%) (Figure 2. A). The results showed that the best degradation efficiency of 92.89% was achieved after 6 h at pH=3, at a concentration of 5 ppm  $\text{ClO}_2$ , while at the same pH and at a concentration of 10 ppm  $\text{ClO}_2$  slightly lower efficiency of the degradation was achieved (87.44%). On the other pH values, 7 and 9 and at a concentration of 5 ppm  $\text{ClO}_2$ , satisfactory degradation efficiency was not observed (at pH=7, after 24 h, 67.57%; at pH=9, after 24 h, 59.24%) (Figure 2. B), but at a concentration of 10 ppm  $\text{ClO}_2$ , at pH 7 and 9 somewhat higher degradation efficiency was achieved (at pH=7, after 24 h, 82.25%; at pH=9, after 24 h, 83.19%) (Figure 2. B). Degradation products analysis and their toxicity evaluation was done using NS sample with the best degradation efficiency, e.g. by treating NS sample with 5 ppm  $\text{ClO}_2$  at pH=3 during 6 h.



**Figure 2.** Degradation efficiency of nicosulfuron: at concentrations 5 and 10 ppm  $\text{ClO}_2$  under light and dark (A) and at different pH values (B)

Analysis of TFSM samples showed that at a concentration of 5 ppm  $\text{ClO}_2$  in the dark high efficiency of degradation was not achieved, while in the light at the same concentration of chlorine dioxide, somewhat better efficiency of degradation was achieved, but it was still not satisfactory (in the dark, after 24 h, 34.38%; in the light, after 24 h, 50.83%) (Figure 3. A). At a concentration of 10 ppm  $\text{ClO}_2$  in the dark, efficiency of the degradation was not satisfactory, while in the light good degradation efficiency was achieved (in the dark, after 24 h, 46.75%; in the light, after 24 h, 73.18%) (Figure 3. A). Satisfactory degradation efficiency was not achieved at all observed pH values and at a concentration of 5 ppm  $\text{ClO}_2$  (at pH=3, after 24 h, 55.86%; at pH=7, after 24 h, 36.96%; at pH=9, after 24 h, 46.29%) (Figure 3. B). However, at a concentration of 10 ppm  $\text{ClO}_2$  and at all pH values relatively good degradation efficiency was achieved, but lower compared to degradation of TFSM with  $\text{ClO}_2$  in the light (at pH=3, after 24 h, 67.23%; at pH=7, after 24 h, 61.36%; at pH=9, after 24 h, 67.26%) (Figure 3. B).



**Figure 3.** Degradation efficiency of thifensulfuron-methyl: at concentrations 5 and 10 ppm  $\text{ClO}_2$  under light and dark (A) and at different pH values (B)

For analysis of degradation products and their toxicity, sample with best degradation efficiency was used, i.e. TFMS sample treated with 10 ppm ClO<sub>2</sub> after 24 h without pH value adjustment.

For the same samples ecotoxicological analysis was performed using *Daphnia Magna*. The data obtained indicate that degradation products of the NS sample, as well as TFMS sample have lower toxicity than the starting herbicides and may be classified in a category III (Toxic unit (TU) = 1-10; TU = 1/LC<sub>50</sub>) (Table 1), as acute toxic on a scale from I to V [21].

**Table 1.** Results of toxicity of degradation products of the herbicides

Sample	LC <sub>50</sub> (%, v/v) 48h
NS: 10 ppm NS + 5 ppm ClO <sub>2</sub> + pH=3 + 6 h	78.92
TFMS: 10 ppm TFMS + 10 ppm ClO <sub>2</sub> + light + 24 h	73.56

## CONCLUSION

Degradation of sulfonylurea herbicides, nicosulfuron and thifensulfuron-methyl (10 ppm) was studied in deionized water under light and dark conditions with different dosage of chlorine dioxide, different time of degradation and at different pH values of solutions. It was found that the degradation of herbicides with chlorine dioxide happens in the dark and in the light and at all pH values. The most efficient degradation of TFMS was obtained in the light at a concentration of 10 ppm of ClO<sub>2</sub>, and it was 73%, while in the case of NS the most effective degradation was achieved at concentration of 5 ppm of ClO<sub>2</sub> at a pH=3 and it was 93%. Toxicological analysis showed that the resulting degradation products of herbicides have lower toxicity compared to the starting herbicides and may be classified in a category III, as well as acute toxic on a scale of I to V. Further research will tend to reducing of toxicity.

## Acknowledgements

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