

5th Metallurgical & Materials Engineering Congress of South-East Europe Trebinje, Bosnia and Herzegovina 7-10th June 2023



CONGRESS PROCEEDINGS

MME SEE

CONGRESS 2023

5th Metallurgical & Materials Engineering Congress of South-East Europe Trebinje, Bosnia and Herzegovina 7-10th June 2023

CONGRESS PROCEEDINGS

Main Organizer

The Association of Metallurgical Engineers of Serbia

Co-organizers

Institute for Technology of Nuclear and Other Mineral Raw Materials in Belgrade, Serbia;

The Faculty of Technology and Metallurgy at the University of Belgrade, Serbia;

The Faculty of Technology at the University of Banja Luka, Bosnia and Herzegovina;

The Faculty of Metallurgy at the University of Zagreb in Sisak, Croatia;

The Faculty of Natural Sciences and Engineering at the University of Ljubljana, Slovenia;

The Faculty of metallurgy and technology at the University of Podgorica, Montenegro.

CONGRESS PROCEEDINGS - MME SEE 2023

5th Metallurgical & Materials Engineering Congress of South-East Europe

Editors:

Dr. Miroslav Sokić,

Institute for Technology of Nuclear and Other Mineral Raw Materials

Dr. Branislav Marković

Institute for Technology of Nuclear and Other Mineral Raw Materials

prof. Dr. Vaso Manojlović

Faculty of Technology and Metallurgy, University of Belgrade

Technical editor:

M. Sc. Gvozden Jovanović

Institute for Technology of Nuclear and Other Mineral Raw Materials

Published and printed by:

Association of Metallurgical Engineers of Serbia (AMES)

Kneza Miloša 9/IV,

11000 Belgrade

Serbia

For the publisher:

AMES president Dr. Miroslav Sokić

Circulation:

120 copies

ISBN 978-86-87183-32-2

GOLD SPONSOR





SILVER SPONSOR







vacuum cryotechnics electron microscopy





Scientific Committee

- Miroslav Sokić, Serbia, president
- Marija Korać, Serbia, vice president
- Sanja Martinović, Serbia, vice president
- Aleksandra Daković, Serbia
- Ana Kostov, Serbia
- Bernd Friedrich, Germany
- Borislav Malinović, Bosnia and Herzegovina
- Boštjan Markoli, Slovenia
- Branislav Marković, Serbia
- Corby Anderson, USA
- Dragomir Glišić, Serbia
- Diagoinii Giisic, Serb
- Duško Minić, Serbia
- Efthymios Balomenos, Greece
- Hakan Atapek, Turkey
- Hasan Avdušinović, Bosnia and Herzegovina
- Jarmila Trpčevska, Slovakia
- Jasna Stajić-Trošić, Serbia
- Jovana Ružić, Serbia
- Karlo Raić, Serbia
- Kemal Delijić, Montenegro
- Lijun Zhang, China
- Ljubica Radović, Serbia
- Martin Debelak, Slovenia
- Mile Đurđević, Austria
- Miljana Popović, Serbia
- Mirjam Jan Blažić, Slovenia
- Miroslav Ignjatović, Serbia
- Nada Štrbac, Serbia
- Natalija Dolić, Croatia
- Nebojša Tadić, Montenegro
- Nenad Radović, Serbia
- Pasquale Daniele Cavaliere, Italy
- Petar Uskoković, Serbia
- Rossita Paunova, Bulgaria
- Srećko Manasijević, Serbia
- Srećko Stopić, Germany
- Tatjana Volkov-Husović, Serbia
- Vaso Manojlović, Serbia
- Veljko Đokić, Serbia
- Vesna Maksimović, Serbia
- Vladan Ćosović, Serbia
- Zdenka Zovko-Brodarac, Croatia
- Željko Kamberović, Serbia

Organizing Committee

- Branislav Marković, Serbia, president
- Vaso Manojlović, Serbia, vice president
- Aleksandar Jovanović, Serbia
- Gvozden Jovanović, Serbia
- Milena Obradović, Serbia
- Mladen Bugarčić, Serbia
- Nela Vujović, Serbia
- Nikola Kanas, Serbia
- Stefan Dikić, Serbia

Reviewer Committee

- Aleksandar Jovanović, Serbia
- Aleksandar Savić, Serbia
- Aleksandra Daković, Serbia
- Blažo Lalević, Serbia
- Bojan Međo, Serbia
- Boštjan Makroli, Slovenia
- Branislav Marković, Serbia
- Branko Matović, Serbia
- Dragana Živoinović, Serbia
- Dragana Radovanović, Serbia
- Dragomir Glišić, Serbia
- Dušica Pešević, Bosnia and Herzegovina
- Gvozden Jovanović, Serbia
- Ivana Cvijović-Alagić, Serbia
- Jelena Avdalović, Serbia
- Jelena Lović, Serbia
- Jovana Perendija, Serbia
- Karlo Raić, Serbia
- Kemal Delijić, Montenegro
- Ksenija Nešić, Serbia
- Maja Đolić, Serbia
- Maja Obradović, Serbia
- Marija Ercegović, Serbia
- Marija Korać, Serbia
- Marina Jovanović, Bosnia and Herzegovina
- Milica Pošarac Marković, Serbia
- Milisav Ranitović, Serbia
- Miljana Popović, Serbia
- Miroslav Sokić, Serbia
- Mladen Bugarčić, Serbia
- Nebojša Nikolić, Serbia
- Nenad Radović, Serbia
- Rada Petrović, Serbia
- Silvana Dimitrijevic, Serbia
- Srđan Matijašević, Serbia
- Srećko Stopić, Germany
- Stevan Dimitrijević, Serbia
- Suzana Filipović, Serbia
- Tatjana Volkov-Husović, Serbia
- Vaso Manojlović, Serbia
- Vladan Ćosović, Serbia
- Zoran Anđić, Serbia
- Zoran Stević, Serbia
- Željko Kamberović, Serbia

REMOVAL OF MESOTRIONE BY HETEROGENEOUS PHOTOCATALYTIC TREATMENT USING UV-VIS LAMP AS LIGHT SOURCE

Jovana Bošnjaković¹, Nataša Knežević², Aleksandar Marinković³, Srećko Manasijević¹, Andrija Savić², Milena Milošević⁴

e-mail: jovana.bosnjakovic@li.rs

- 1- Research and Development Institute Lola L.T.D., Kneza Višeslava 70A, 11030 Belgrade, Serbia, 2- University of Belgrade, "VINČA" Institute of Nuclear Sciences National Institute of the Republic of Serbia, Mike Petrovića Alasa 12-14, 11351 Belgrade, Serbia,
- 3- University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia,
 4- University of Belgrade, Institute of Chemistry, Technology and Metallurgy, National Institute of the Republic of Serbia, Njegoševa 12, 11000 Belgrade, Serbia

Population growth, the development of agriculture, industry, and mining, caused the creation of an increasing amount of wastewater. Due to the discharge of wastewater, without prior treatment, the quality of water resources is impaired. Polluting substances, such as pesticides, have a negative impact on human health and the environment. Heavy pollution of both surface and underground water is one of the biggest problems associated with the use of pesticides. They reach human organisms indirectly via agricultural products. Most pesticides are more or less toxic, some of them are highly soluble in water. In recent years, special attention has been paid to the development of methods for the treatment of wastewater contaminated with pesticide residues, in order to partially reduce or eliminate their further impact on humans, plants, and the environment. Among many processes, the photocatalytic degradation process has proven to be a very effective process for the removal of pesticides from wastewater. Photocatalytic degradation implies the breakdown of various types of toxic organic substances into simpler molecules, such as ions, water, etc.

In this paper, the photocatalytic degradation of the pesticide mesotrione (MS) using ZnO photocatalyst is presented. The degradation of the pesticide compound was studied using Shimadzu 1800 analytical UV-VIS spectroscopy. As a replacement for UVC radiation, a solar-imitated irradiation Ultra Vitalux (UV) lamp (300W) was used. Degradation kinetics follows pseudo-first order. After 240 minutes, the MS was completely degraded.

Keywords: mesotrione, photocatalytic degradation, pesticides, UV-VIS

Introduction

Pesticides are chemical substances or biological agents that being used against insects, weeds, microorganisms that cause diseases or are harmful in some other way [1]. They have become an essential tool in agriculture and in urban life, and it is impossible to imagine modern agricultural production without them [2]. Pesticides have been used in agriculture for more than fifty years, and about five hundred different pesticides are registered [3]. Pesticides are divided into different classes based on their application, way of penetrating the body, chemical structure, mechanism of action [3]. Main classes arephysiotropes, hemosterilants, fungicides, bactericides, insecticides, and herbicides [4]. The range of preparations based on these chemical substances used in agriculture is constantly changing, systematically renewed, poorly effective substances are replaced by more effective and less dangerous for the environment. Most pesticides are more or less toxic. Due to their high toxicity, carcinogenicity, and bioaccumulation, they can have a very negative influence on human health when combined with other pollutants found in wastewater [2]. Also, most have a negative impact on aquatic organisms, like atrazine. Atrazine is one of the most popular herbicides from the triazine group, whose primary purpose was to control weeds in corn fields. However, since 2007, atrazine has been banned in the countries of the European Union, and mesotrione is being used instead to control weeds in corn fields [5]. Mesotrione is a benzoyl-ciclohexanedione herbicide used to control a variety of broad leaf weeds, particularly in corn production. It is relatively new and insufficiently researched on the market. Mesotrione is stable in water in the presence of light (DT50) for about 90 days, based on a 2003 European Commission report [5].

One of the biggest problems that occur when using pesticides is the large pollution of surface and underground waters. Groundwater is of great importance for life on Earth, so its pollution is a big problem. With the use of pesticides, only a small part attacks the target harmful organism, while the rest ends up in underground, in surface water and soil. Through direct use, crop washing off, and runoff from the soil surface, they enter waterbodies and soil [2]. In order to protect the environment, the priority is to reduce the use of pesticides and to replace high-risk active substances with less risky ones [1]. Special attention is paid to the development of methods that would help to purify waters polluted by pesticide residues in order to, at least partially, reduce or eliminate their further negative impact on humans, plants, animals and the environment in general. The two most popular methods for treating wastewater are photodegradation and biological treatment [6]. Biological treatment means the degradation of fungi and bacteria in natural waters and soil. Photochemical methods have several advantages, such as the shorter time of the purification process, they are more efficient compared to biological methods [5]. In addition, because pesticides are so hazardous to microorganisms, wastewater cannot be treated by biological methods and its biodegradation is not possible [7]. Photodegradation is the most suitable technique for purifying waters polluted by pesticides. Organic radicals are produced as a result of oxidation-degradation processes that occur through the photodegradation process.

The goal of this work is the photocatalytic degradation of mesotrione with the help of a UV-Vis lamp as a source of consciousness in deionized water, using a ZnO photocatalyst.

Materials and methods

Chemicals

Mesotrione and ZnO were purchased from Sigma Aldrich and were used without any further purification.

Photocatalytic degradation experiment

Photocatalytic degradation of mesotrione (MS) was performed with the help of ZnO photocatalyst. A glass thermostated cylindrical reactor, with a volume of 100 cm^3 , was used for the experiment. The temperature of the reaction was constant (25 °C), thanks to the double walls in which the thermostatic water circulates.

The initial concentration of the MS solution was 2 ppm, while the mass of the ZnO catalyst was 0.067 g/L. During the irradiation process, the suspension was mixed on a magnetic stirrer (500 rpm), whereby an even distribution of ZnO particles was achieved. In order to protect it from daylight, the apparatus is placed in a digester. Sampling was done in certain time intervals. Through a nylon filter (Cronus, 13 mm, $0.22\,\mu m$), the samples were filtered after they were taken from the reactor. With the help of a UV-Vis spectrophotometer (Shimadzu 1800), the change in pesticide concentration was monitored in the range from 200 to 400 nm, in quartz cuvettes with an optical path of 1 cm. At 225 nm, the degradation kinetics were determined.

In the processes of photocatalytic degradation, as a measure of the catalytic activity of ZnO, the degree of mesotrione removal and the reaction rate constant (k) were used.

The degradation rate constant is pseudo-first order and is determined using the Langmuir-Hinshelwood kinetic model.

$$\ln\left(\frac{C}{C_0}\right) = -kt$$
(1)

where k is the pseudo-first-order rate constant.

Results and discussion

The removal of used pesticide mesotrione (Figure 1) in wast water using commercial catalyst cinc oxide and UVA lamps as simulated sunlight irradiation was studied. Besides, in the absence of UV-Vis radiation, as well as catalyst the degradation process was not observed. The efficiency of the photocatalytic process will decrease, if the initial concentration of the substrate increases, because the number of adsorbed MS molecules on the surface of the catalyst increases [5].

Figure 1 Chemical structure of the mesotrione

The influence of the ZnO photocatalyst concentration on the photocatalytic degradation of mesotrione was shown on Figure 2.

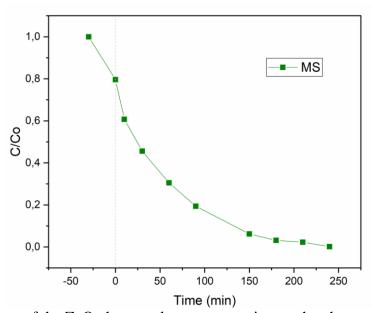


Figure 2 The influence of the ZnO photocatalyst concentration on the photocatalytic degradation of mesotrione

Based on the results shown, it can be concluded that about 68% degraded after 30 minutes, while 98% degraded after 240 minutes. Also, the photoactivity of the semiconductor decreases, and as a result, organic molecules and catalyst particles have the ability to absorb light.

Based on the literature data, it can be concluded that the photocatalytic efficiency of TiO₂ Degussa P25 and ZnO in the photocatalytic degradation of mesotrione is similar [5]. Also, it is important to mention that it has been previously reported that based on a review of the literature, it was determined that during irradiation with the help of sunlight, mesotrione is completely degraded in two days, with the help of both catalysts, while in the absence of them, only 60% is degraded over 6 months, while in the dark it is not degraded at all [5]. Based on the results presented, it can be concluded that the UV/catalyst treatment is the most effective for the removal of mesotrione.

Conclusion

The subject of this work was the photocatalytic degradation of mesotrione with the help of a UV-Vis lamp, as a source of sunlight. ZnO nanogranular catalyst was used during the study of photocatalytic degradation. The change in MS concentration was monitored on a UV-Vis spectrophotometer. The degradation kinetics is pseudo-first order. After 240 minutes MS has completely degraded. Based on the presented results, it can be seen that MS was successfully degraded with the help of ZnO photocatalyst, on the basis of which we can conclude that the applied system has a sustainable path in the following research.

Acknowledgement

This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract Nos. 451-03-47/2023-01/200066, 451-03-47/2023-01/200017, 451-03-47/2023-01/200026, 451-03-47/2023-01/200135)

Reference

- 1. Carvalho, F. P. "Pesticides, environment, and food safety. *Food Energy Secur* 6 (2): 48–60." (2017). https://doi.org/10.1002/fes3.108.
- 2. Kaur, Rajveer, Gurjot Kaur Mavi, Shweta Raghav, and Injeela Khan. "Pesticides classification and its impact on environment." *Int. J. Curr. Microbiol. Appl. Sci* 8, no. 3 (2019): 1889-1897. https://doi.org/10.20546/ijcmas.2019.803.224.
- 3. Sakkas, V. A., Paola Calza, A. D. Vlachou, Claudio Medana, Claudio Minero, and T. Albanis. "Photocatalytic transformation of flufenacet over TiO₂ aqueous suspensions: Identification of intermediates and the mechanism involved." *Applied Catalysis B: Environmental* 110 (2011): 238-250. https://doi.org/10.1016/j.apcatb.2011.09.006.
- 4. Marican, Adolfo, and Esteban F. Durán-Lara. "A review on pesticide removal through different processes." *Environmental Science and Pollution Research* 25 (2018): 2051-2064. https://doi.org/10.1007/s11356-017-0796-2.
- 5. Šojić, Daniela V., Dejan Z. Orčić, Dragana D. Četojević-Simin, Vesna N. Despotović, and Biljana F. Abramović. "Kinetics and the mechanism of the photocatalytic degradation of mesotrione in aqueous suspension and toxicity of its degradation mixtures." *Journal of Molecular Catalysis A: Chemical* 392 (2014): 67-75. http://dx.doi.org/10.1016/j.molcata.2014.04.033.
- 6. Syafrudin, Muhammad, Kristanti, Risky Ayu, Yuniarto, Adhi, Hadibarata, Tony, Rhee, Jongtae, Al-onazi, Wedad A., Algarni, Tahani Saad, Almarri, Abdulhadi H.,and Al-Mohaimeed, Amal M.," Pesticides in Drinking Water—A Review," International Journal of Environmental Research and Public Health 18 (2021):468-483, https://doi.org/10.3390/ijerph18020468.

7. Elfikrie, Nurulizani, Yu Bin Ho, Siti Zulfa Zaidon, Hafizan Juahir, and Eugenie Sin Sing Tan. "Occurrence of pesticides in surface water, pesticides removal efficiency in drinking water treatment plant and potential health risk to consumers in Tengi River Basin, Malaysia." *Science of the Total Environment* 712 (2020): 136540. https://doi.org/10.1016/j.scitotenv.2020.136540

СІР - Каталогизација у публикацији Народна библиотека Србије, Београд 669(082)(0.034.2) 66.017/.018(082)(0.034.2) 621.7/.9(082)(0.034.2)



METALLURGICAL & Materials Engineering Congress of South-East Europe (5; 2023; Beograd)

Congress Proceedings [Електронски извор] / 5th Metallurgical & Materials Engineering Congress of South-East Europe MME SEE Congress 2023, Trebinje, Bosnia and Herzegovina 7-10th June 2023; [[organized by] The Association of Matallurgical Engineers of Serbia [AMES] ... [et al.]]; [editors Miroslav Sokić, Branislav Marković, Vaso Manojlović]. - Belgrade: Association of Metallurgical Engineers of Serbia (AMES), 2023 (Belgrade: Association of Metallurgical Engineers of Serbia (AMES)). - 1 USB fleš memorija; 1 x 6 x 9 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 120. - Preface / Miroslav Sokić. - Bibliografija uz svaki rad.

ISBN 978-86-87183-32-2

а) Металургија -- Апстракти б) Технички материјали -- Зборници в) Наука о материјалима -- Зборници г) Металопрерађивачка индустрија -- Зборници

COBISS.SR-ID 117307657

