УНИВЕРЗИТЕТ У БАЊОЈ ЛУЦИ
UNIVERSITY OF BANJA LUKA
ТЕХНОЛОШКИ ФАКУЛТЕТ
FACULTY OF TECHNOLOGY

PROCEEDINGS

OCTOBER 21-22, 2022

ACADEMY OF SCIENCES AND ARTS
OF THE REPUBLIC OF SRPSKA,
BANJA LUKA, REPUBLIC OF SRPSKA, B&H

INTERNATIONAL SCIENTIFIC CONFERENCE

XIV CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA

XIV CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA

BOOK OF PROCEEDINGS

Publisher:
University in Banjaluka, Faculty of Technology

Editorial board:
Borislav Malinović, PhD, dean

Design and computer processing
Pero Sailović, PhD
MSc Marina Rakanović
MSc Đorđe Vujčić

CIP - Каталогизација у публикацији
Народна и универзитетска библиотека
Републике Српске, Бања Лука

66(082)
661:663/664(082)
502(082)

CONFERENCE of Chemists, Technologists and Environmentalists of Republic of Srpska (14 ; 2023)
[Book of proceedings] : international scientific conference / XIV Conference of Chemists, Technologists and Environmentalists of Republic of Srpska ; [editorial board Borislav Malinović]. - Banja Luka : University in Banjaluka, Faculty of Technology, 2023 ([S.l : s.n.]). - 313 стр. ; 24 cm

Библиографија уз сваки рад.

ISBN 978-99938-54-98-2

COBISS.RS-ID 137637377

Organizing Committee:

PhD Pero Sailović, president, PhD Darko Bodroža, general secretary, M.Sc Maja Milijaš secretary, M.Sc Dajana Dragić, M.Sc Branka Ružičić, M.Sc Marina Rakanović, M.Sc Maja Katić, Sanda Pilipović, M.Sc Nebojša Gorgi, Biljana Vasić, Sanja Novaković, M.Sc Jovanka Kotur

***Students*:** Vladimir Ivković, Jovan Savić, Nevena Janjić, Bojana Milinković, Danijela Lazić

Scientific Committee:

Dr Božana Odžaković, president, University of Banja Luka, **B&H**, Dr Nada Štrbac, co-president, Univesity of Belgrade, **Serbia**, Dr Borislav Malinović, University of Banja Luka, **B&H**, Dr Vlada Veljković, University of Niš, **Serbia**, Dr Todor Vasiljević, Victoria University Melbourne, **Australia,** Dr Sanja Mahović-Poljačak, University of Zagreb, **Croatia**, Dr Csaba Horvath, University Obuda, Budapest, **Hungary**, Dr Mihail Kochubovski, University of Skopje, **Macedonia**, Dr Massimiliano Fenice, Universityt Della Tuscia, **Italy**, Dr Georgij Petriaszwili, Warshav University of Technology, **Poland**, Dr Mira Vukcević, University of Monte Negro, **Monte Negro**, Dr Ondrej Panák, University of Pardubice, **Czech Republic**, , Dr Pospiech Matej, University of Veterinary and Pharmaceutical Sciences, Brno, **Czech Republic**, , Dr Dani Dordevic, University of Veterinary and Pharmaceutical Sciences, Brno, **Czech Republic,** Dr Iskren Spiridonov, University of Chemical Technology and Metallurgy, **Bulgaria**, Dr Laura Benea, West University of Timisoara, **Romania**, Dr Savvas G. Vassiliadis, University of Piraeus, **Greece**, Dr Helena Prosen, University of Ljubljana, **Slovenia**, Dr Srecko Stopic, RWTH University Aachen, **Germany**, Dr Maria Iosune Cantalejo, UPNA, **Spain**, Dr Jurislav Babić, University of Osijek, **Croatia**, Dr Svetozar Milosavić, University of Kosovska Mitrovica, **Serbia**, Dr Petar Uskoković, University of Belgrade, **Serbia**, Dr Mitja Kolar, University of Ljubljana, **Slovenia**, Dr Dragiša Savić, , University of Niš, **Serbia**, Dr Dragan Vujadinović, University of East Sarajevo, **B&H**, Dr Biljana Pajin, University of Novi Sad, **Serbia**, Dr Sead Ćatić, University of Tuzla, **B&H**, Dr Husein Vilić, University of Bihać, **B&H**, Dr Sanjin Gutić, University of Sarajevo, **B&H**, Dr Goran Trbić, University of Banja Luka, **B&H**, Dr Milica Balaban, University of Banja Luka, **B&H**, Dr Ljiljana Vukić, University of Banja Luka, **B&H**, Dr Ljiljana Topalić-Trivunović, University of Banja Luka, **B&H**, Dr Slavica Sladojević, University of Banja Luka, **B&H**, Dr Pero Dugić, University of Banja Luka, **B&H**, Dr Zoran Kukrić, University of Banja Luka, **B&H**, Dr Slavica Grujić, University of Banja Luka, **B&H**, Dr Milorad Maksimović, University of Banja Luka, **B&H**, Dr Branka Rodić-Grabovac, University of Banja Luka, **B&H**, Dr Rada Petrović, University of Banja Luka, **B&H**, Dr Dragana Grujić, University of Banja Luka, **B&H**, Dr Svjetlana Janjić, University of Banja Luka, **B&H**, Dr Zora Levi, University of Banja Luka, **B&H**, Dr Ladislav Vasilišin, University of Banja Luka, **B&H**

NOTE:

The authors have full responsibility for the originality and content of thier own papers

УНИВЕРЗИТЕТ У БАЊОЈ ЛУЦИ
UNIVERSITY OF BANJA LUKA
ТЕХНОЛОШКИ ФАКУЛТЕТ
FACULTY OF TECHNOLOGY

International scientific conference

"XIV CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA"

under the auspices of

MINISTRY OF SCIENTIFIC AND TECHNOLOGICAL DEVELOPMENT, HIGHER EDUCATION AND INFORMATION SOCIETY

MINISTRY OF AGRICULTURE, FORESTRY AND WATER MANAGEMENT

ACADEMY OF SCIENCES AND ARTS OF THE REPUBLICA OF SRPSKA

Original scientific article

PHOTOCATALYTIC DECOMPOSITION OF DIFENOCONAZOLE FROM WASTEWATERS

Jovana Bošnjaković[1], Nataša Knežević[2], Srećko Manasijević[1], Aleksandar Jovanović[3], Mladen Bugarčić[3], Aleksandar Marinković[2]

[1]Research and Development Institute Lola L.T.D., Kneza Višeslava 70A, 11030 Belgrade, Serbia
[2]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia
[3]Institute for Technology of Nuclear and Other Raw Materials, Bulevar Franše d'Eperea 86, 11000 Belgrade, Serbia

Abstract

Due to the rapid development of industry and growth of population, water consumption is increased. Beside this, releasing of xenobiotics, which represent significant pollutants into watercourse, like heavy metal ions, pesticides, paints, and solvents, made this problem much bigger. Therefore, they can enter into aquatic organisms directly from industrial plants or into human bodies indirectly through agricultural products. New technologies, including photocatalytic decomposition, are necessary for wastewater treatment as a highly efficient and low-cost process. Photocatalysis implies the degradation of various types of harmful organic substances to simple molecules such as CO_2, SO_2, ions, and water. The applied process has no detrimental effect on the environment and does not require additional chemicals for precipitation of the products. In this work, photodegradation of the pesticide difenoconazole (DFC) using a TiO_2-based photocatalyst was examined using doubled wall thermoregulated quartz reactor. As a replacement for UVC radiation, solar imitated Ultra Vitalux (UV) lamp (300W) was used. Determination of DFC concentration was performed using a UV method. Degradation kinetics follows pseudo-first order. After 120 minutes, the DFC was completely degraded. Chemical oxygen demand (COD) also confirmed that successfully indicating that this process can be used in treating of industrial wastewater.

Keywords: photodegradation, xenobiotics, environmental, DFC, wastewater.

Introduction

Pesticides are products of biological or chemical origin intended for the protection of plants and animals from harmful insects, diseases. The use of pesticides has a negative impact on the ecosystem in which they are applied. In order to maintain agricultural production, reducing the use of pesticides is of great importance. They are used in agriculture for more than fifty years. About five hundred different pesticides have been registered (Sakkas et al., 2011). The classification is made depending on the purpose, chemical structure, mechanism of action (Sakkas et al., 2011). They can be divided into herbicides, insecticides, fungicides, bactericides, physiotropes, hemosterilants (Marican & Durán-Lara, 2018). In the Republic of Serbia, usage of pesticides in agricultural production is still in small quantities. In recent decades, pesticides are increasingly present in underground, surface and drinking water (Moore et al., 2007; Palma et al., 2009; Šunjka, 2012). Together with other pollutants, which are present in wastewater, they can have a very severe impact on human health due to high toxicity, carcinogenicity, bioaccumulation (Eriksson et al., 2007). Less than 0.1% of the applied amount reaches the target organisms and about 99.9% is lost to the environment (Pimentel, 1995). They get into water and soil through direct use, washing off crops, and runoff from the soil surface

(Jing et al., 2011). In order to improve the protection of the environment, the management of pesticide residues represents a special challenge.

Pesticides-polluted waters is a major problem for the environment and requires systematic monitoring. The need for the development of new technologies that could be used in the treatment of wastewater contaminated with pesticides arose due to their long-term degradation by photolysis and high stability in the environment (Bavcon Kralj et al., 2007). Photodegradation and biological treatment are the widely used techniques in wastewater treatment (Oller et al., 2011). Biological treatment (BT) is the degradation of pollutants in the soil and natural waters by fungi and bacteria. However, due to the low efficiency and long duration of the purification process, BT is not widely used in industry (Hincapié et al., 2005). Also, due to the high toxicity of pesticides towards microorganisms, wastewater can not be treated by biological methods and its biodegradation is not possible (Chiron et al., 2000). The most suitable technique for removing pesticides from wastewater is photodegradation. During the photodegradation process, oxidation-degradation reactions take place during which organic radicals are generated. The intermediate radicals that were formed during the degradation process are captured by dissolved molecular oxygen and are further guided through peroxyl radicals, thus increasing the efficiency of the degradation process (Tomašević et al., 2009). The advantage of this process compared to other processes is that it results in a complete transformation of harmful substances (Tomašević et al., 2009).

The aim of this work is to investigate the possibility of removing DFC from wastewater using the photocatalytic degradation process utilizing TiO_2 as a photocatalyst.

Materials and Methods

Degradation of DFC by means of heterogeneous photocatalysis was carried out with the help of TiO_2 P25 (Degussa) photocatalyst. For the purposes of the experiment, a cylindrical glass thermostated reactor with a volume of 100 cm^3 was used. The double walls in which the thermostatic water circulates in the reactor made it possible to maintain the reaction temperature.

The initial concentration of DFC solution was 15 ppm, while the mass of TiO_2 was 10 mg. The suspension is mixed during the irradiation process on a magnetic stirrer (500 rpm). In this way, an even distribution of TiO_2 particles was achieved. The apparatus was placed in a digester, in which protection from daylight was provided. In certain time intervals, sampling was carried out for the purposes of analytical testing. After sampling from the reactor, filtration was performed through a nylon filter (Cronus, 13 mm, 0.22 μm).

The change in pesticide concentration was monitored on a UV/Vis spectrophotometer (Shimadzu 1800) in the range from 200 to 400 nm, in quartz cuvettes with an optical path of 1 cm. Residual concentrations were sampled at certain time intervals (0, 10, 20, 30, 60, 90 and 120 min). Degradation kinetics were determined at 235 nm.

The degree of removal of DFC and the reaction rate constant (k) were used as a measure of the catalytic activity of TiO_2 in photocatalytic degradation processes. With the help of the Langmuir-Hinshelwood (Li et al., 2021) kinetic model, the pseudo-first-order degradation rate constant was determined.

$$\ln c/c_0 = -k \cdot t \quad (1)$$

where k is the reaction constant, pseudo first order.

Results and discussion

Absorption spectra of adsorbate medium given as a series are provided in the Figure 1. As it can be seen from the Figure 1, absorption maximums lowers as the contact time increases. The changes in

the adsorption spectra during the degradation of DFC during 2h of irradiation are presented. The rate of photocatalytic degradation of DFC is influenced by its initial concentration. Research has shown that the speed of the process decreases with increasing pesticide concentration. In Figure 2, it can be seen how the initial concentration of DFC affects the photocatalytic degradation, in the presence of the optimal concentration of TiO_2. An increase in the initial concentration of the substrate leads to an increasing number of DFC molecules adsorbed on the surface of the catalyst, which leads to a decrease in the efficiency of the photocatalytic process (Nezamzadeh-Ejhieh & Moeinirad, 2011). Also, organic molecules have the ability to absorb light, as well as catalyst particles, and this leads to a decrease in the photoactivity of semiconductors (Nezamzadeh-Ejhieh & Moeinirad, 2011).

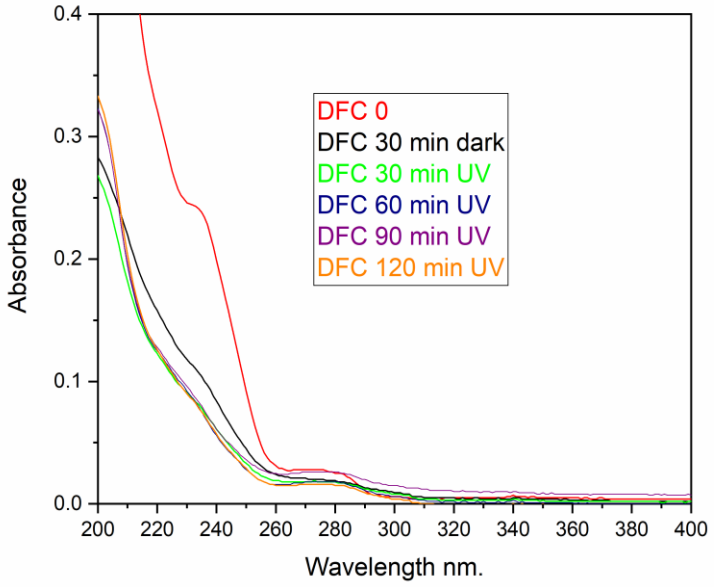

Figure 1. UV adsorption spectrum of DFC in the presence of 10 mg/L TiO_2

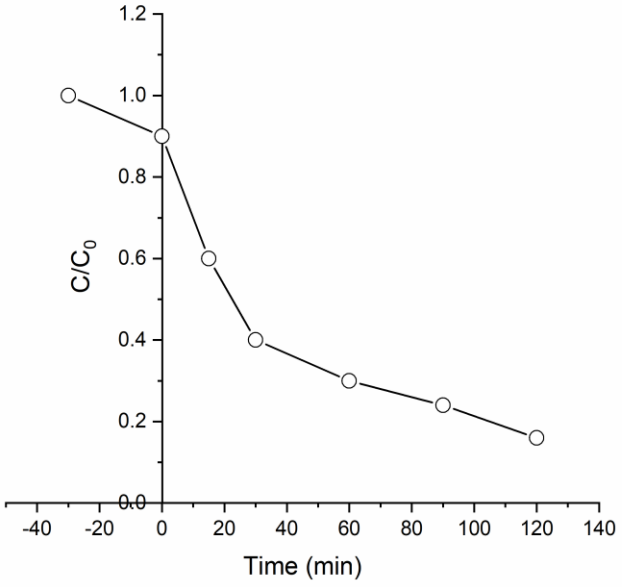

Figure 2. Effect of DFC concentration on the rate of photocatalytic degradation in wastewater

Conclusion

The subject of this work was the removal of DFC from wastewater by photocatalytic degradation. Photocatalytic degradation was studied with the help of nanogranulometric photocatalyst TiO_2 P25 (Degussa), in a thermostated quartz reactor. The change in DFC concentration was monitored on a UV/Vis spectrophotometer. The degradation kinetics is pseudo-first order. After 120 minutes, DFC was fully degraded. Based on the presented results, it can be concluded that DFC was successfully degraded from wastewater with the help of TiO_2 photocatalyst, which implies that applied system has a viable path in future investigation and optimization.

Acknowledgements: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No., 451-03-1270/2022-14/2685, 451-03-68/2022-14/200066, 451-03-68/2022-14/200023, 451-03-68/2022-14/200135).

References

Bavcon Kralj, M., Černigoj, U., Franko, M. & Trebše, P. (2007). Comparison of photocatalysis and photolysis of malathion, isomalathion, malaoxon, and commercial malathion-Products and toxicity studies. *Water Research*, *41*(19), 4504–4514. https://doi.org/10.1016/j.watres.2007.06.016

Chiron, S., Fernandez-Alba, A., Rodriguez, A. & Garcia-Calvo, E. (2000). Pesticide chemical oxidation: State-of-the-art. *Water Research*, *34*(2), 366–377. https://doi.org/10.1016/S0043-1354(99)00173-6

Eriksson, E., Baun, A., Mikkelsen, P. S. & Ledin, A. (2007). Risk assessment of xenobiotics in stormwater discharged to Harrestrup Å, Denmark. *Desalination*, *215*(1–3), 187–197. https://doi.org/10.1016/j.desal.2006.12.008

Hincapié, M., Maldonado, M. I., Oller, I., Gernjak, W., Sánchez-Pérez, J. A., Ballesteros, M. M. & Malato, S. (2005). Solar photocatalytic degradation and detoxification of EU priority substances. *Catalysis Today*, *101*(3-4 SPEC. ISS.), 203–210. https://doi.org/10.1016/j.cattod.2005.03.004

Jing, J., Liu, M., Colvin, V. L., Li, W. & Yu, W. W. (2011). Photocatalytic degradation of nitrogen-containing organic compounds over TiO_2. *Journal of Molecular Catalysis A: Chemical*, *351*, 17–28. https://doi.org/10.1016/j.molcata.2011.10.002

Li, T., Abdelhaleem, A., Chu, W., Pu, S., Qi, F. & Zou, J. (2021). S-doped TiO_2 photocatalyst for visible LED mediated oxone activation: Kinetics and mechanism study for the photocatalytic degradation of pyrimethanil fungicide. *Chemical Engineering Journal*, *411*(July 2020), 128450. https://doi.org/10.1016/j.cej.2021.128450

Marican, A. & Durán-Lara, E. F. (2018). A review on pesticide removal through different processes. *Environmental Science and Pollution Research*, *25*(3), 2051–2064. https://doi.org/10.1007/s11356-017-0796-2

Moore, M. T., Lizotte, R. E., Knight, S. S., Smith, S. & Cooper, C. M. (2007). Assessment of pesticide contamination in three Mississippi Delta oxbow lakes using Hyalella azteca. *Chemosphere*, *67*(11), 2184–2191. https://doi.org/10.1016/j.chemosphere.2006.12.026

Nezamzadeh-Ejhieh, A. & Moeinirad, S. (2011). Heterogeneous photocatalytic degradation of furfural using NiS-clinoptilolite zeolite. *Desalination*, *273*(2–3), 248–257. https://doi.org/10.1016/j.desal.2010.12.031

Oller, I., Malato, S. & Sánchez-Pérez, J. A. (2011). Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review. *Science of the Total Environment*, *409*(20), 4141–4166. https://doi.org/10.1016/j.scitotenv.2010.08.061

Palma, P., Kuster, M., Alvarenga, P., Palma, V. L., Fernandes, R. M., Soares, A. M. V. M., López de Alda, M. J., Barceló, D. & Barbosa, I. R. (2009). Risk assessment of representative and priority pesticides, in surface water of the Alqueva reservoir (South of Portugal) using on-line solid phase extraction-liquid chromatography-tandem mass spectrometry. *Environment International*, *35*(3), 545–551. https://doi.org/10.1016/j.envint.2008.09.015

Pimentel, D. (1995). Amounts of pesticides reaching target pests: Environmental impacts and ethics. *Journal of Agricultural and Environmental Ethics*, *8*(1), 17–29. https://doi.org/10.1007/BF02286399

Sakkas, V. A., Calza, P., Vlachou, A. D., Medana, C., Minero, C. & Albanis, T. (2011). Photocatalytic transformation of flufenacet over TiO_2 aqueous suspensions: Identification of intermediates and the mechanism involved. *Applied Catalysis B: Environmental*, *110*, 238–250. https://doi.org/10.1016/j.apcatb.2011.09.006

Šunjka, D. B. (2012). *Ostaci atrazina i njegovih degradacionih produkata u podzemnim vodama Srbije*. Doktorska disertacija, Poljoprivredni fakultet, Univerzitet u Novom Sadu.

Tomašević, A. V., Avramov Ivić, M. L., Petrović, S. D., Jovanović, M. B. & Mijin, D. Ž. (2009). A study of the electrochemical behaviour of methomyl on a gold electrode in a neutral electrolyte. *Journal of the Serbian Chemical Society*, *74*(5), 573–579. https://doi.org/10.2298/JSC0905573T