UNIVERSITY OF NIŠ
Faculty of Technology, Leskovac

BOOK OF ABSTRACTS

13th SYMPOSIUM

" Novel Technologies and Economic Development "

Leskovac, October, 18 - 19, 2019

Faculty of Technology, Leskovac

Publisher: Faculty of Technology, Leskovac

For the Publisher: Prof. Ljubiša Nikolić

Editor: Prof. Miodrag Lazić

CIP – Каталогизација у публикацији
Народна библиотека Србије

6(048)

SYMPOSIUM with international participation "Novel Technologies and Economic Development" (13 ; 2019 ; Leskovac)
Book of Abstacts / 13 th Symposium [with international participation] "Novel Technologies and Economic Development" Leskovac, October, 18-19, 2019. ; [organized by] Faculty of Technology, Leskovac [and] Serbian Academy of Sciences and Arts (SANU), Branch in Niš] ; [editor Miodrag Lazić]. - Leskovac : Faculty of Technology, 2019 (Leskovac : Makos print). – 223 str. : ilustr. ; 24 cm

Na vrhu nasl. str.: University of Niš. - Tiraž 180. - Registar.

ISBN 978-86-89429-35-0

а) Технологија -- Апстракти б) Технолошки прогрес -- Привредни развој -- Апстракти

COBISS.SR-ID 279403020

Print: MAKOS-PRINT, Leskovac; 2019.
Printing: 180

Proofreader: Biljana Mitić Stanković
Paging and graphical design: Vesna Marinković

ISBN 978-86-89429-35-0

The authors are grateful to the Ministry of Education, Science, and Technological Developme of the Republic of Serbia for funding the study (Projects No. III 46008 and 172013

PHOTOCHEMICAL PROCESSES FOR REMOVAL OF CARBAMATE PESTICIDES FROM WATER

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Carbamates are a large group of pesticides which have been extensively used over th past almost seventy years. It is a very large family whose members are effective a insecticides, herbicides, and fungicides, but they are most commonly used a insecticides. More than 50 carbamates are known, and they are a group of pesticide with a potential to affect the functioning of the nervous sistem. Because of the widespread use in agriculture and relatively good solubility in water, carbama pesticides can contaminate both surface and ground water resources.

Methomyl and carbofuran are carbamate pesticides and they have been in use fo many years. Methomyl (IUPAC name S-methyl N-(methylcarbamoyloxy)thioacetimidate) is an insecticide/acaricide used for control of a wide range of insects and spider mites on fruits, vines, olives, hops, vegetable ornamentals, field crops, cucurbits, flax, cotton, tobacco, soya beans, etc. It can als be used for control of flies in animal and poultry houses and dairies. Formulation type for this active ingredient are SL, SP, and WP. Carbofuran (IUPAC name: 2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) is a systemic insecticide wit predominantly contact and stomach action. It is used for control of soil-dwelling an foliar-feeding insects and nematodes on vegetables, ornamentals, beet, maize sorghum, sunflower, oilseed rape, potato, alfalfa, peanut, soya bean, sugar cane, rice cotton, coffee, cucurbits, tobacco, lavender, citrus, vine, strawberry, banana mushroom and other crops. This active ingredient is prepared as FS, GR, SC and WP formulation.

Considering different methods of remediation of methomyl and carbofuran residue from water, the present study will focus on reaction pathways and the mechanism o their photodegradation. The most beneficial photochemical processes for removal o methomyl and carbofuran residues from water tested in the study were found to be th Advanced Oxidation Processes (AOPs), including heterogeneous photocatalysis wit the semiconductor oxide TiO_2, as well as with ZnO. Direct UV photolysis was als investigated. Heterogeneous photo-Fenton process was also applied.

Photolysis uses light only for degradation of different environmental contaminants including pesticide residues. Direct irradiation promotes pesticides into their excite singlet state, and such excited state can then undergo homolysis, heterolysis o photoionization processes.

The AOPs, which utilize hydroxyl radicals for environmental remediation, have bee successfully employed for degradation of organic compounds, including pesticides The AOP_s include catalytic and photochemical methods and have H_2O_2, O_3 or O_2 a the oxidant. The principal active species in this system is the hydroxyl radical $^{\bullet}OH$ which is an extremely reactive and non-selective oxidant for organic contaminants. Th main advantage of AOP_s is complete mineralization of many organic pollutants whic breaks them into water, CO_2, mineral salts, and non-toxic compounds. AOP_s involv

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different homogeneous and heterogeneous photocatalytical processes. Homogeneous photocatalytic oxidation employs various oxidation systems (Fenton reagent, H_2O_2, O_3, etc), either alone or in combination with UV, visible or natural solar light. Heterogeneous photocatalytical processes, named heterogeneous photocatalysis, involve a combination of UV or solar light, various catalysts (TiO_2, ZnO, ZnS, ZrO_2, CdS, SnO_2, WO_3, etc.) and different oxidants (H_2O_2, $K_2S_2O_8$, KIO_4, $KBrO_3$, etc.).

This presentation comprises photolytic and photocatalytic removal of methomyl and carbofuran at low concentration from different types of water, upon the activity of UV, visible or natural solar light, in the presence of TiO_2 and ZnO catalysts, and using Fe-ZSM-5-zeolite and AlFe-pillared montmorillonite. The effects of different operational parameters, such as the initial concentration of pesticides and catalysts, pH, and initial salt concentration, were studied. Also, a comparative study on degradation of carbofuran and its commercial product Furadan 35-ST at 315-400 nm in ZnO aqueous suspension will be presented in order to assess the effects of inert ingredients present in the commercial product on carbofuran photodegradation.

The rate of photodecomposition of pesticides was measured using UV spectroscopy and high-performance liquid chromatography (HPLC), while their mineralization was investigated by ion chromatography (IC) and total organic carbon analysis (TOC). Photodegradation products of pesticides were identified based on the results of high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) and gas chromatography-mass spectrometry (GC-MS), and their photodegradation pathways are proposed.