RSEE

9th Regional Symposium on Electrochemistry South-East Europe

Book of Abstracts

ASEEE Association of South-East European Electrochemists

Serbian Chemical Society

University of Novi Sad Faculty of Technology Novi Sad

Novi Sad, Serbia - June 3 to 7, 2024

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

621.357/.359(048)(0.034.2)
544.6(048)(0.034.2)
620.193/.197(048)(0.034.2)
66.087(048)(0.034.2)
543.25(048)(0.034.2)

REGIONAL Symposium on Electrochemistry South-East Europe (9 ; 2024 ; Novi Sad)
Book of Abstracts [Elektronski izvor] / 9th Regional Symposium on Electrochemistry South-East Europe, RSE-SEE, Novi Sad, Serbia - June 3 to 7, 2024 ; [editors Branimir Grgur, Igor Pašti, Aleksandar Dekanski]. - Belgrade : Serbian Chemical Society, 2024 (Belgrade : Development and Research Centre of Graphic Engineering, Faculty of Technology and Metallurgy). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 20. - Bibliografija uz većinu apstrakata.

ISBN 978-86-7132-085-6

а) Електрохемијско инжењерство -- Апстракти б) Галванотехника -- Апстракти в) Електрохемија -- Апстракти г) Електрохемијске реакције -- Апстракти д) Антикорозиона заштита -- Апстракти ђ) Аналитичка електрохемија -- Апстракти

COBISS.SR-ID 145235465

9th Regional Symposium on Electrochemistry - South-East Europe

Book of Abstracts

Publisher
Serbian Chemical Society, Karnegijeva 4/III, Belgrade, Serbia
https://shd.org.rs; E-mail: office@shd.org.rs

For Publisher
Prof. Dr. Dušan Sladić, president of the Society

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Page layout, design, and cover
Dr. Aleksandar Dekanski

ISBN 978-86-7132-085-6
https://doi.org/10.5281/zenodo.11194247
Circulation: 20 copies
Printing: RICGI, Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

Belgrade, june 2024

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Biochar-modified carbon paste electrode as an advanced material for electrochemical investigation of pesticide mancozeb

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Biochar (BC) is a carbonaceous material produced from naturally abundant raw materials (biomasses – mostly from the agricultural tailing and forestry ecosystem wastes or municipal wastes) *via* a pyrolysis process. With the growth of green chemistry concepts, the preparation and application of BC have attracted strong interest owing to the combination of fascinating physicochemical properties including large surface area, high porosity, surface charge, sustainability and low-cost which are beneficial in various fields, such as the remediation of polluted environments, soil amendments, wastewater treatment, and electrochemical sensors [1-3]. From the various electrode materials available nowadays, the classical carbon paste electrode (CPE) has widespread popularity as a working electrode due to its unique properties such as wide potential range, long-time stability, good conductivity, renewable surface, ease of preparation and modification, whereby the modifying agents can be added directly to the paste, either to the material in its final state or during its preparation [4]. In this work, CPE was bulk modified with biochar obtained from the hardwood source (BC-CPE) with the aim to develop a reliable alternative method for the determination of broad-spectrum fungicide mancozeb (MCZ). Cyclic voltammetric experiments showed that the oxidation of MCZ is irreversible and an adsorption control process at the BC-CPE surface. In the next step, a simple, sensitive and selective electroanalytical method for the determination of MCZ using differential pulse adsorptive stripping voltammetry (DP-AdSV) was proposed. Optimization of various experimental parameters was carried out including the pH of the supporting electrolyte, the amount of the modifier and the preconcentration step. At pH 7.0 of Britton-Robinson buffer, with accumulation potential of -0.2 V and accumulation time of 30 s, a linear relationship between MCZ concentration and peak current intensity was established between 0.025 and 2.78 μg mL^{-1}, the relative standard deviation did not exceed 3%, while achieved detection limit in the model solution was 7.5 ng mL^{-1}. The BC-CPE showed adequate selectivity for MCZ in the presence of various interfering compounds. The obtained results indicate that BC-CPE with an optimized DP-AdSV method could be applied for the trace-level electroanalytical determination of MCZ in real samples.

Acknowledgement: This research was supported by the Science Fund of the Republic of Serbia, #10810, Sustainable solutions in environmental chemistry: exploring biochar potential–EnviroChar.

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Exploring biochar potential for electrochemical sensing of pesticide maneb

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The great potential of biochar as a low-cost material obtained from renewable resources for the development of electrochemical sensors is recognized for the analysis of various electroactive organic compounds [1-3]. In this study, an electrochemical sensor based on biochar derived from a hardwood source as an environmentally sustainable material is used as a modifier of carbon paste electrode (CPE) to improve the voltammetric determination of pesticide maneb (MAN). Maneb belongs to the group of dithiocarbamate fungicides that could be used for the treatment of fruits and vegetables. The increase of dithiocarbamates metabolite concentrations in the environment may disrupt protein synthesis and metabolism. Therefore, a rapid, simple, and sensitive analytical approach for the analysis of MAN is needed [4]. Biochar (BC) material was prepared from hardwood at two temperatures, 400 °C (BC400) and 700 °C (BC700), and characterized by scanning electron microscopy, and specific surface area analysis. Obtained results showed a porous structure of BC with relatively high surface areas, *i.e.* 176 $m^2 g^{-1}$ at 400°C and 284 $m^2 g^{-1}$ at 700 °C. As it is expected, BC produced at high temperatures has a higher surface area and better conductivity [5]. Due to the good catalytic properties of BC as a material, an enhanced sensitivity of electrochemical sensors based on BC could be achieved [6]. Accordingly, observed oxidation peak intensities have shown the differences between an unmodified CPE, CPE modified with a BC400 (BC400-CPE), and CPE modified with a BC700 (BC700-CPE) for the analysis of MAN whereby BC700-CPE provides the most favourable analytical response of target analyte. Cyclic voltammetric investigations revealed that the electrode reaction is irreversible and controlled by the adsorption of MAN at the surface of the working electrode, which led to an optimization of the differential pulse adsorptive stripping voltammetric (DP-AdSV) method for quantifying MAN in a model solution. Under the optimized experimental parameters (10.0 % BC700 in CPE, Britton-Robinson buffer pH 7.0, E_{acc} = -0.2 V, t_{acc} = 90 s), the oxidation peak of MAN (at 0.55 V) showed a linear response in a concentration range from 0.049 to 1.84 μg mL^{-1} with evaluated limit of detection of 0.015 μg mL^{-1} and relative standard deviation of 3.23 %. The obtained results open the possibility of exploring BC700-CPE potential for MAN determination in environmental samples.

Acknowledgement: This research was supported by the Science Fund of the Republic of Serbia, #10810, Sustainable solutions in environmental chemistry: exploring biochar potential–EnviroChar.

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