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

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INTRODUCTION

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 [4]. In this work, CPE was bulk modified with biochar (BC-CPE) with the aim to develop a reliable alternative method for the determination of broad-spectrum fungicide mancozeb (MCZ) (**Fig. 1**).

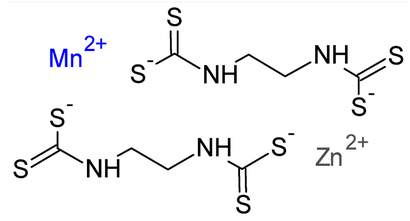

Fig. 1. Chemical structure of MCZ

EXPERIMENTAL

The stock solution of MCZ (25.0 μg mL^{-1}) was prepared in 10% DMSO. Britton-Robinson (B-R) buffer was used as supporting electrolyte. BC was obtained from the hardwood source *via* a pyrolysis process at 700 °C. Voltammetric measurements were performed on an AUTOLAB PGSTAT 12 (Ecochemie, The Netherlands) operated *via* GPES 4.9 software. A three-electrode system was applied with an unmodified or BC-modified CPE as the working electrode, a saturated calomel electrode (SCE) as a reference, and a platinum wire as an auxiliary electrode.

RESULTS AND DISCUSSION

Cyclic voltammetric experiments showed that the oxidation of MCZ is irreversible and an adsorption control process at the BC-CPE surface (**Fig. 2**).

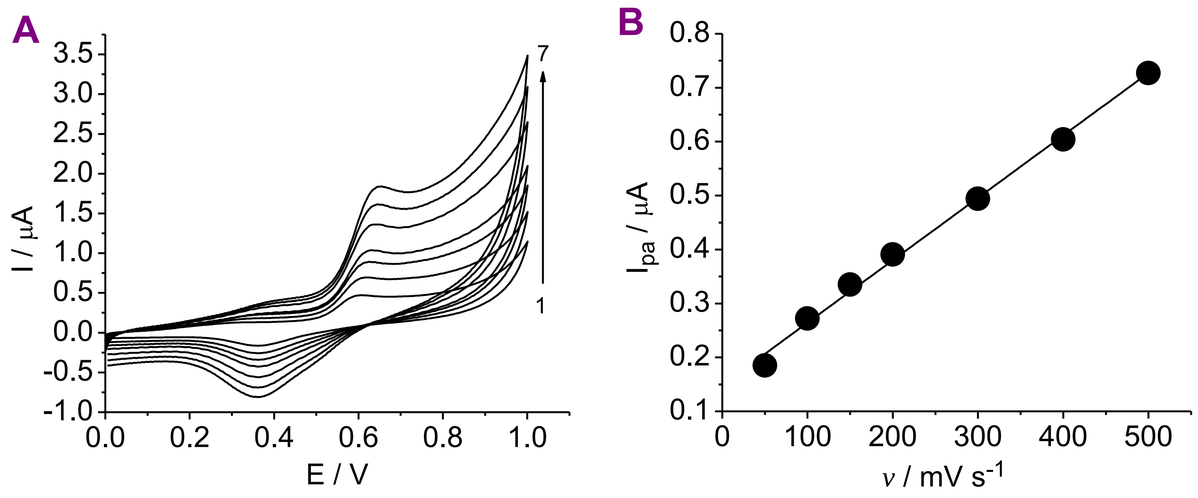

Fig. 2. CVs of 4.17 μg mL^{-1} MCZ at pH 7.0 at various ν (A): 1)→7) corresponds to 50, 100, 150, 200, 300, 400 and 500 mV s^{-1}, respectively, and the effect of variation of ν on the I_{pa} (B)

A simple, sensitive and selective differential pulse adsorptive stripping voltammetric (DP-AdSV) method for the determination of MCZ 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. The most intensive oxidation peak of MCZ was obtained at CPE modified by 10% of BC (**Fig. 3**) and reaches its maximum intensity at pH 7.0, whereby the optimal adsorption parameters were E_{acc} = -0.2 V and t_{acc} = 30 s.

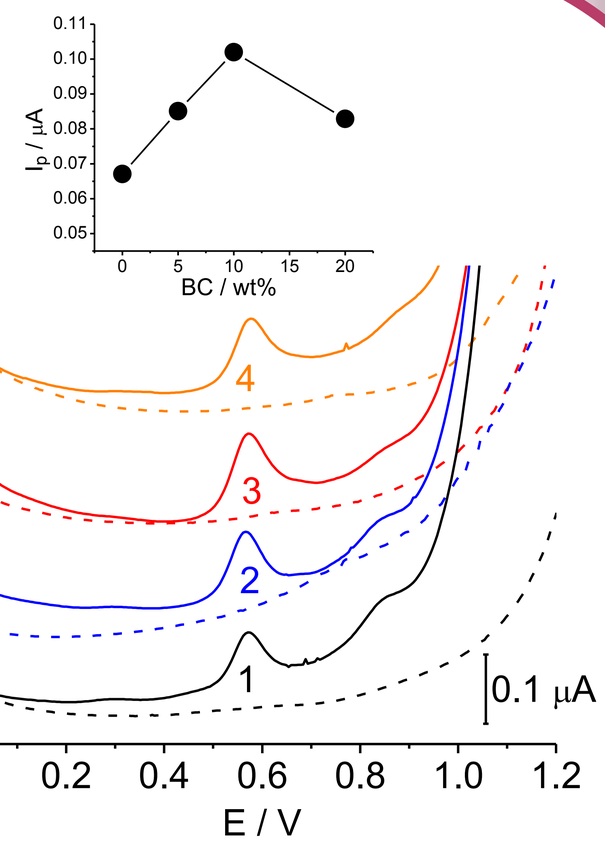

Fig. 3. Effect of varying amounts of BC in CPE on the peak intensity of 1.19 μg mL^{-1} MCZ at pH 7.0. DPV curves 1-4: 1) unmodified CPE; 2) 5; 3) 10; 4) 20 wt% of BC in CPE

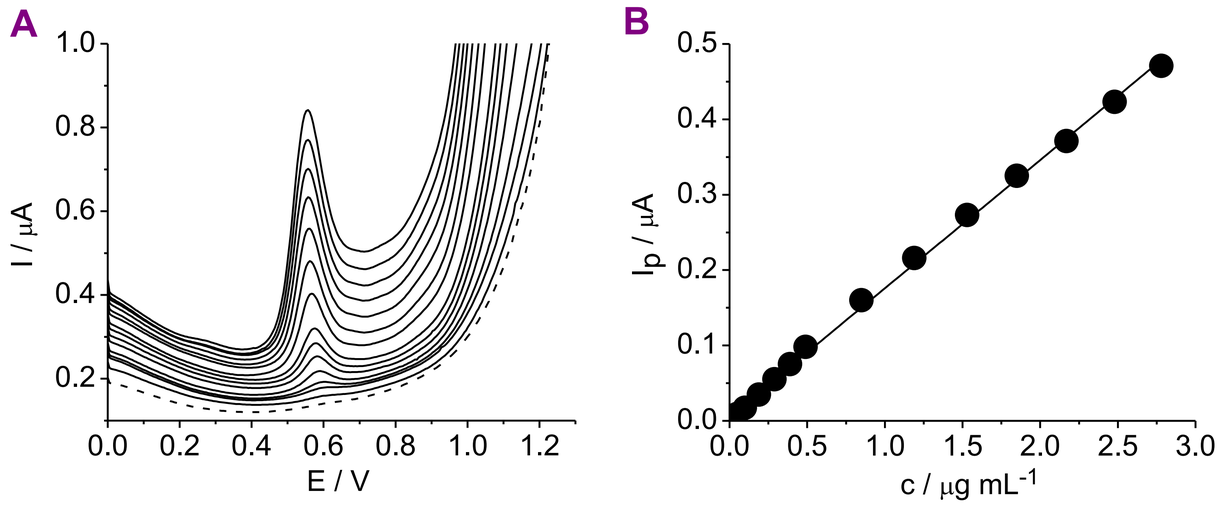

Fig. 4. DP-AdSV signals obtained for increasing concentrations of MCZ (from 0.025 to 2.78 μg mL^{-1}) at BC-CPE in B-R buffer pH 7.0 (A). Corresponding calibration curve (B).

Under optimized conditions, a linear relationship between MCZ concentration and peak current intensity was established between 0.025 and 2.78 μg mL^{-1} (**Fig. 4**), 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 practical applicability of BC-CPE was demonstrated through trace-level electroanalytical determination of MCZ in spiked river water and wastewater samples with good repeatability and recovery.

References

1. D. Spanu, G. Binda, C. Dossi, D. Monticelli, *Microchem. J.* **159** (2020) 105506.
2. Y. Li, R. Xu , H. Wang, W. Xu, L. Tian, J. Huang, C. Liang, Y. Zhang, *Biosensors* **12** (2022) 377.
3. B.N. Sulastri, K.A. Madurani, F. Kurniawan, *J. Nano-Electron. Phys.* **15** (2023) 03005.
4. K. Kalcher, I. Švancara, M. Buzuk, K. Vytras, A. Walcarius, *Monatsh. Chem.* **140** (2009) 861.

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