Green electrochemical sensor based on biochar for quantification of selected pesticides in aqueous solutions

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INTRODUCTION

The sustainable and green electrode material biochar (BC) is a highly porous and carbon-rich material that could act as a catalytic material to enhance the analytical performance of BC-based electrochemical sensors [1, 2].

The modification of carbon paste electrode (CPE) with sustainable electrode materials is highly encouraged due to the improved selectivity and sensitivity for trace level analysis of various electroactive analytes such as fungicides mancozeb (MCZ, Fig. 1A) and maneb (MAN, Fig. 1B) which could be found in the environment [3].

In the present work, previously synthesized BC was investigated as bulk modifier of CPE for novel MCZ and MAN sensor design.

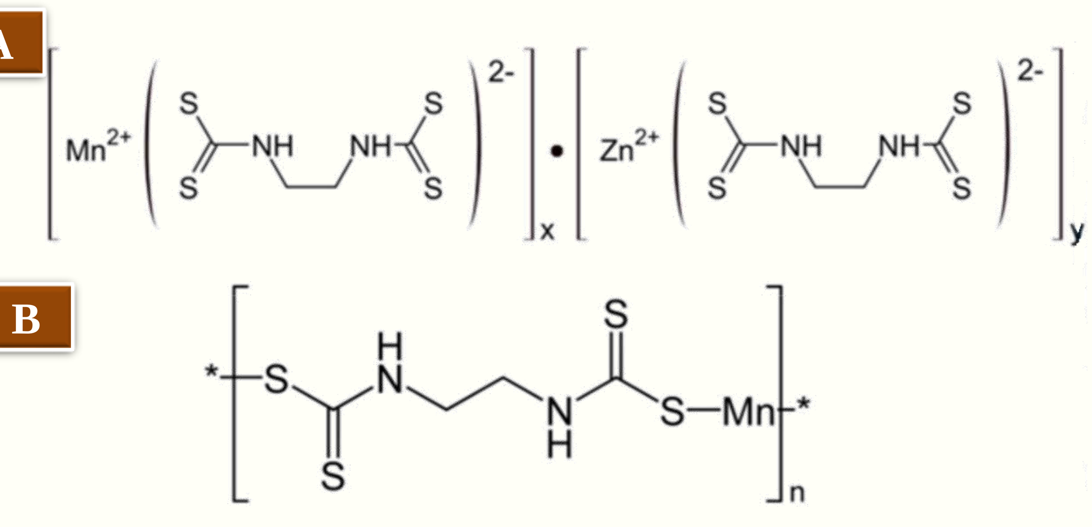

Fig. 1. Chemical structure of MCZ (A) and MAN (B)

EXPERIMENTAL

The MCZ or MAN analytical standard was dissolved in 10% DMSO and double distilled water, respectively. Voltammetric measurements were performed on AUTOLAB PGSTAT 12 electrochemical analyzer operated via GPES 4.9 software (Ecochemie, The Netherlands). The voltammetric cell included a three-electrode system with a BC-CPE (10 wt% of BC in CPE) as the working electrode, a saturated calomel electrode (SCE) as a reference, and a platinum auxiliary electrode. BC was synthesized from the hardwood source *via* a pyrolysis process at 700 °C.

Britton-Robinson (B-R) buffer as supporting electrolyte was prepared from 0.04 mol L^{-1} phosphoric acid, boric acid and acetic acid by successive addition of 0.2 mol L^{-1} sodium hydroxide to adjust the pH value of the medium.

RESULTS AND DISCUSSION

The oxidation signal of MCZ or MAN at different pH values (Fig. 2A and Fig. 3A) was recognized and the dependence of the peak intensity (I_p) on the pH value (Fig. 2B and Fig. 3B) indicates that pH 7.0 is optimal. The linear dependence of the peak potential (E_p) on pH can be described by the following equations: E_p = -0.108 pH + 1.33; r = 0.999 (Fig. 2B, inset) and E_p = -0.110 pH + 1.36; r = 0.999 (Fig. 3B, inset). In both cases, at pH values higher than 10 there is a deviation from linearity (Fig. 2B and 3B, inset).

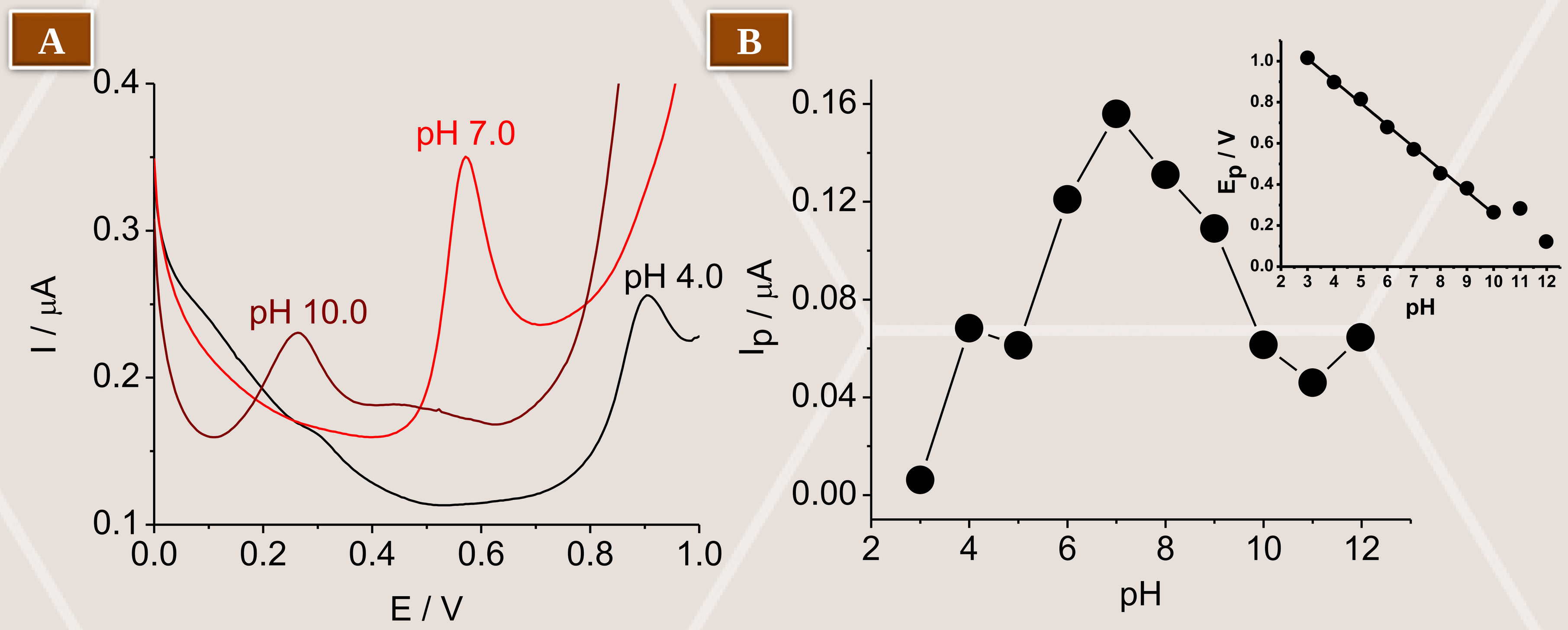

Fig. 2. DP voltammograms in the presence of 1.19 µg mL^{-1} MCZ at selected pH values of B-R buffer (A). Dependence of I_p (B) and E_p (inset, B) of the MCZ peak on pH using BC-CPE

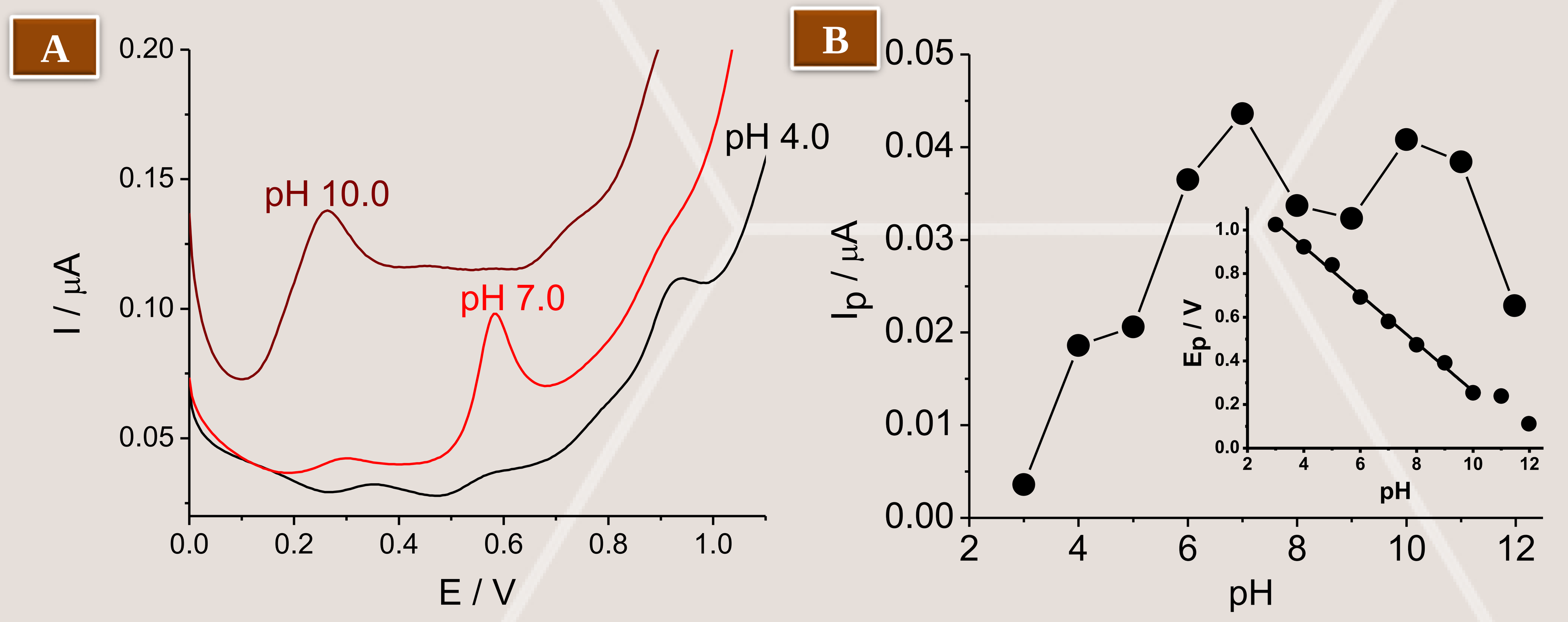

Fig. 3. DP voltammograms in the presence of 1.19 µg mL^{-1} MAN at selected pH values of B-R buffer (A). Dependence of I_p (B) and E_p (inset, B) of the MAN peak on pH using BC-CPE

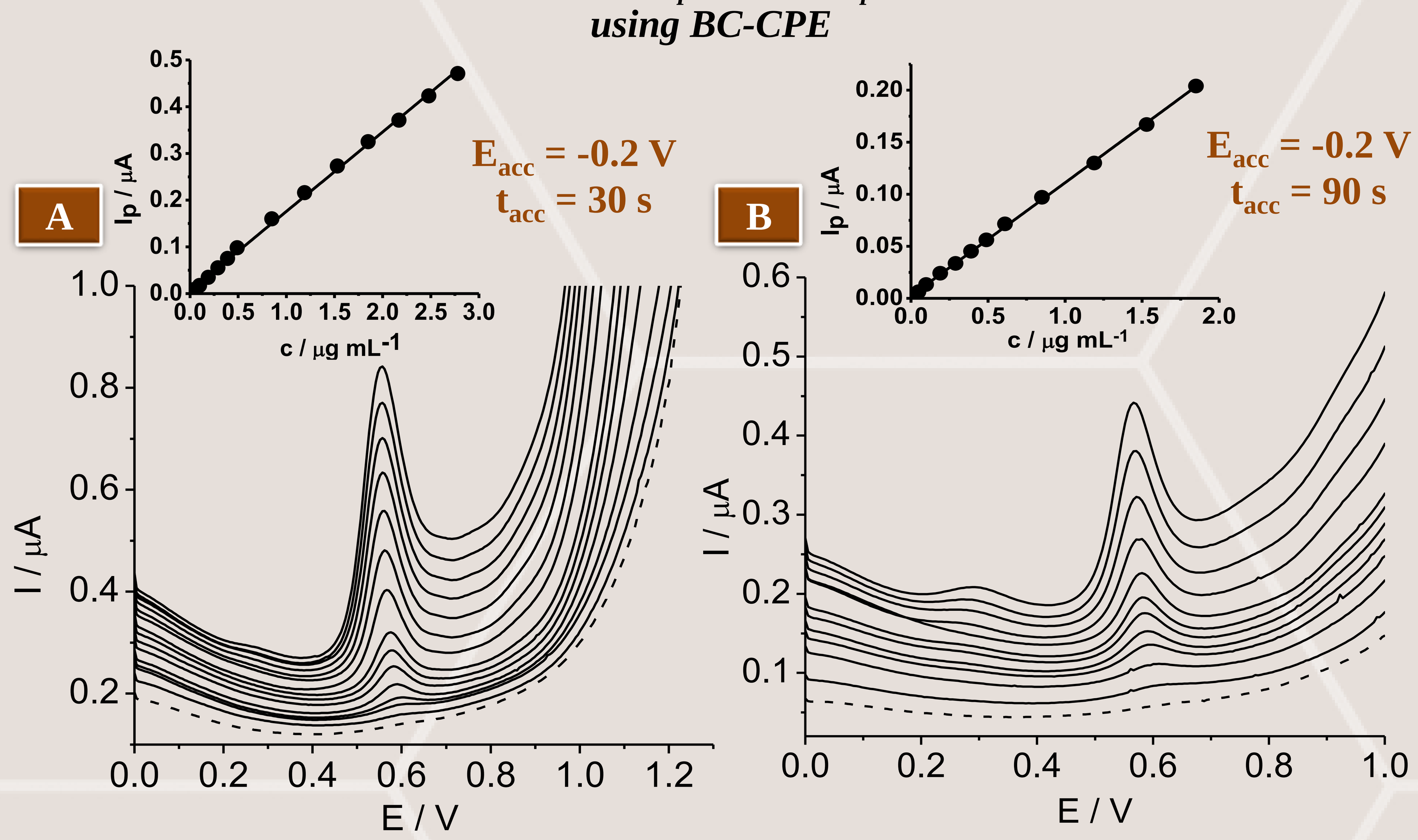

Fig. 4. DPAdSV signals of different concentrations of MCZ (from 0.025 to 2.78 µg mL^{-1}, A) and MAN (from 0.049 to 1.84 µg mL^{-1}, B) at BC-CPE in B-R buffer pH 7.0. Insets: Corresponding calibration curve

BC-CPE and DPAdSV for MCZ and MAN determination (Fig. 4):

- *Good sensitivity: detection limit of 7.5 and 15 ng mL^{-1} MCZ and MAN, respectively.*
- *Good reproducibility: relative standard deviation (n=6) 2.9% for MCZ and 3.2% for MAN analytical signal.*
- *Possibility for monitoring of MCZ and MAN in aquatic environmental samples.*

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