BIOCHAR-BASED ELECTROCHEMICAL SENSORS FOR PESTICIDES DETECTION IN AQUATIC ENVIRONMENT

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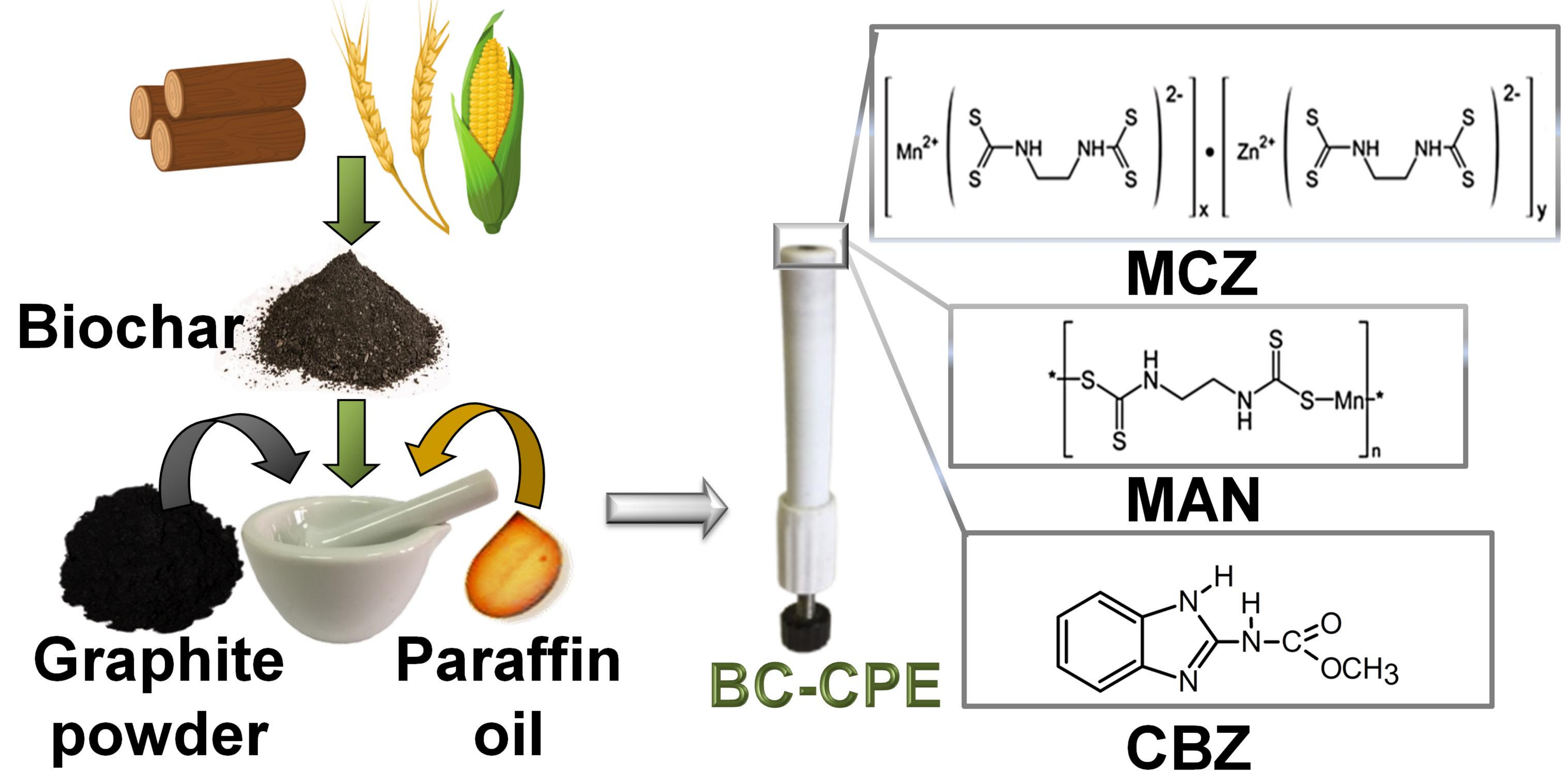
INTRODUCTION

As the research and the applications of electrochemical sensors continue to develop, a single-handed pursuit of accuracy and sensitivity cannot meet the demands of the analysis in many *in situ* or *point-of-care* testing circumstances. More cost-effective, stable, and versatile electrodes, as well as more stable and repeatable sensing strategies, are needed. The peculiar properties of biochar (BC) were exploited for the development of electrochemical sensors in view of its lower environmental footprint compared to the widely investigated synthetic carbonaceous nanomaterials, reaching analogous or even better analytical performances in the field of electrochemical sensing. With the growth of green chemistry concepts, the preparation and application of BC have been receiving increased attention. In addition to its advantages (i.e., amorphous characteristics, large specific surface area, surface charge and good stability, etc.), BC has highly reactive and surface-functionalized spherical and porous structures. Therefore, BC is a good candidate as a material for electrodes fabrication or modification. The aim of the present work was to develop rapid and highly sensitive voltammetric methods based on the use of biochar-modified carbon paste electrodes (BC-CPE) for determination of fungicides mancozeb (MCZ), maneb (MAN) and carbendazim (CBZ).

EXPERIMENTAL

BC from a hardwood (HBC), corn cob (CBC) and wheat straw (WBC) biomass was synthesized *via* pyrolysis process at 400 °C and 700 °C. Unmodified carbon paste electrode (CPE) was prepared from graphite powder and paraffin oil (70:30 (*w/w*)) in a porcelain mortar with a pestle. BC-CPEs were prepared by mixing graphite powder with an appropriate amount of BC and paraffin oil. A three-electrode system was applied with an unmodified or BC-modified CPE as the working electrode, a saturated calomel electrode as a reference, and a platinum wire as an auxiliary electrode. Britton-Robinson (B-R) buffer was used as supporting electrolyte.



RESULTS AND DISCUSSION

Cyclic voltammetry (CV) was applied to investigate electrode features which may pinpoint BC as a promising electrode modification material. CV measurements of MCZ, MAN and CBZ at unmodified CPE and BC-CPEs were performed (Fig. 1). HBC700-CPE showed the most favorable interactions with the MCZ and MAN, while WBC700-CPE had the highest potential for the development of a voltammetric method for CBZ determination. From the investigation in the model solution, the utility of sensitive and selective BC-CPEs (Table 1) has been shifted to real environmental samples and represents a reliable greener analytical tool for fungicides determination in river water, surface water and wastewater samples (Table 2).

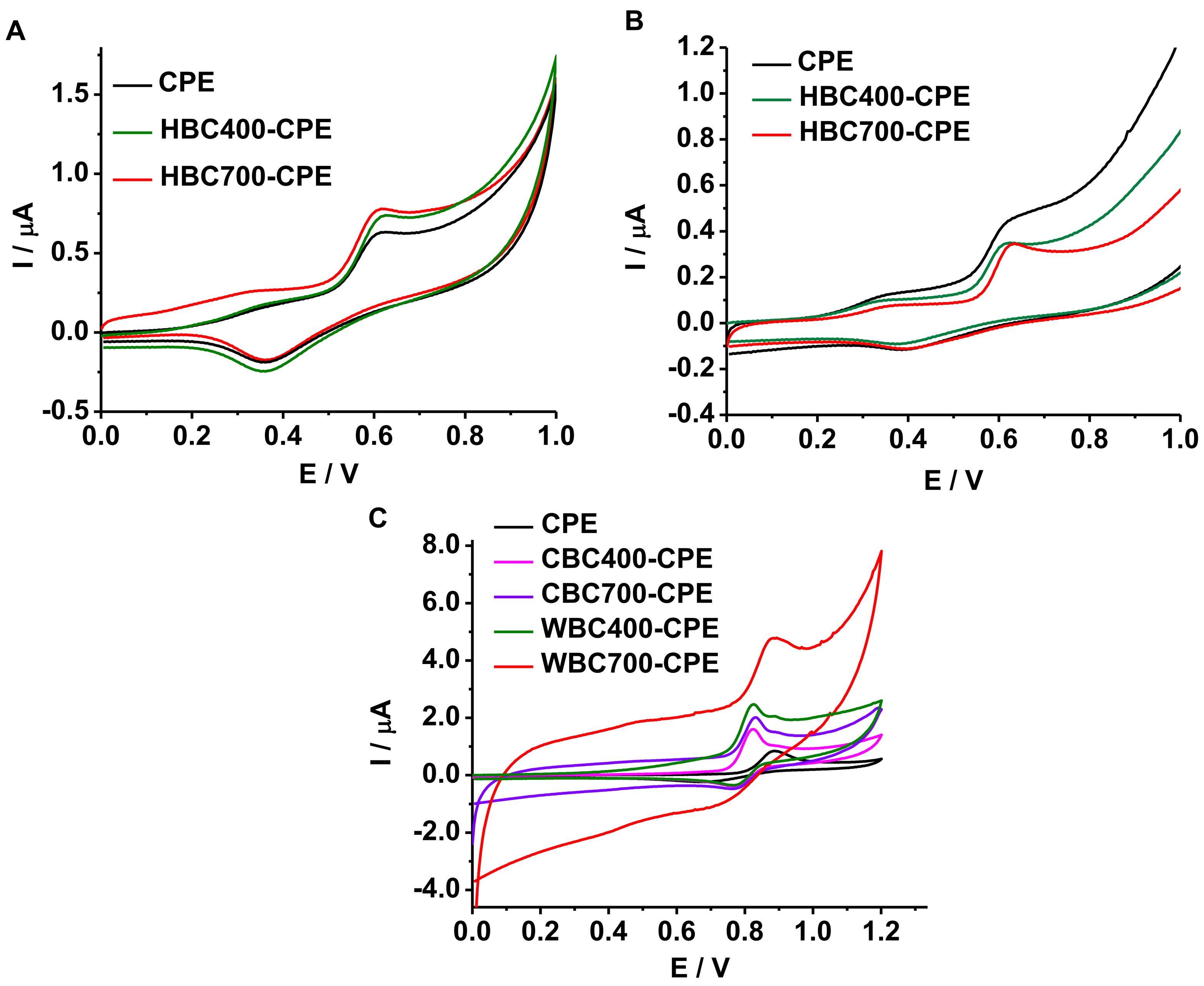


Fig. 1. **CV signals of MCZ (A), MAN (B) and CBZ (C) obtained using unmodified CPE and CPEs modified with 10% of different BCs, *v*=100 mV s^{-1}**

Table 1. **Analytical parameters for the voltammetric determination of MCZ, MAN and CBZ**

Parameters	MCZ	MAN	CBZ
Working electrode	10%HBC700-CPE	10%HBC700-CPE	5%WBC700-CPE
pH of B-R buffer	7.0	7.0	6.0
Method	DP-AdSV	DP-AdSV	SW-AdSV
Concentration range (µg L^{-1})	25–2780	49–1840	1.25-50
Slope (µA L µg^{-1})	0.00017	0.00011	0.033
Intercept (µA)	0.0058	0.0023	0.010
Correlation coefficient	0.999	0.999	0.999
LOD (µg L^{-1})	7.5	15.0	0.38
LOQ (µg L^{-1})	25.0	49.0	1.25
RSD (%)	2.9	3.2	1.2

Table 2. **Determination of MCZ, MAN and CBZ in spiked environmental water samples**

Parameters	MCZ		MAN		CBZ	
Sample	River water	Wastewater	River water	Wastewater	Surface water	Wastewater
Added (µg L^{-1})	198.0	198.0	198.0	198.0	9.98	9.98
Found^{a} (µg L^{-1})	197.3	201.3	197.0	197.6	10.13	9.92
Recovery^{b} (%)	99.6	101.7	99.5	99.8	101.5	99.4
RSD (%)	1.9	1.3	1.0	1.6	2.1	1.5

^{a}*Mean value (n=3)*
^{b}*Recovery = [(Found–Added)/Added] × 100 + 100%*

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