DEVELOPMENT OF A LOW-COST SENSOR FOR METHYLPARABEN DETECTION AND MONITORING

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ABSTRACT

Methylparaben (MP), a widely used preservative in food and personal care products (PCPs), is recognized as a significant emerging contaminant due to its hormone-mimicking properties, posing environmental and health risks. This study developed a low-cost, disposable sensor (DS) modified with biochar and copper nanoparticles (BC-CuNPs) to monitor MP in natural water samples. The sensor was crafted by optimizing a conductive ink composed of graphite, sodium alginate, and ultrapure water. Characterization was performed using Electron Microscopy (EM-SEM), X-ray Dispersive Spectroscopy (EDS), Infrared Spectroscopy (FTIR), Cyclic Voltammetry (CV), and Linear Sweep Voltammetry (LSV). Unmodified sensors showed an irreversible oxidation peak at +835.1 mV *vs.* Graphite. Modification with BC-CuNPs led to a 44 mV reduction in anodic peak potential and a 2.82-fold increase in anodic current (I_{pa}). When modified only with BC, enhancements included a 33 mV decrease in peak potential and a 1.85-fold increase in current response. These findings underscore substantial improvements in the sensor's voltammetric response through these modifications

Keywords: Electrochemical sensor 1. Emerging contaminant 2. Methylparaben 3. Biochar 4. Water 5.

1 INTRODUCTION

Emerging Contaminants (ECs) are substances and microorganisms detected in low concentrations in water, soil, and air. These raise concerns due to the lack of regulatory oversight and their diversity. A 2022 study in Brazil highlighted a significant prevalence of ECs in the Southeast, particularly in São Paulo, where various classes of ECs, including illicit drugs and caffeine [1], were found. Parabens, such as methyl-, ethyl-, propyl-, and butylparabens, fall within these contaminants. Widely used in cosmetics, pharmaceuticals, and foods for their chemical stability and antimicrobial properties against gram-positive bacteria and fungi[2], parabens are commonly found in the urine of pregnant women and their nine-year-old children. Research indicates that exposure to parabens and phenols is associated with premature development of secondary sexual characteristics in children[3]. Chronic exposure to parabens disrupts endocrine systems and is linked to the carcinogenesis of breast cancer, as evidenced by their presence in breast tumor tissues[4]. Methylparaben (MP) is particularly notable as a food preservative and component of several personal care products (PCP). Its hormone-mimicking properties and presence in natural waters pose significant health and environmental risks. Efficient methods for its detection, monitoring, and treatment are urgently needed.

Disposable electrochemical sensors are currently under scientific and technological investigation as a viable solution for analytical detection. They democratize analytical chemistry and environmental biotechnology with their low cost, reliability, portability, and ease of use. These devices are designed to be made from low-cost, biodegradable, or sustainable materials, and are compact, using minimal material in their manufacture.[5] Silva *et al.* demonstrated the effectiveness of paper-based disposable electrochemical sensors for determining chloroquine and escitalopram with excellent sensitivity.[6]

Brazil's commitment to the 17 Sustainable Development Goals (SDGs) set by the UN for 2030, particularly those related to "Drinking water and sanitation" and "Life in water," underscores the need for robust water quality monitoring for both human and animal health. This work proposes a method that not only aims to meet these SDGs but also advances science by creating affordable, disposable electrochemical sensors to monitor contaminants such as methylparaben. This simplified and rapid monitoring technique facilitates the identification of contamination and risk areas, directing efforts toward effective treatment and ensuring all water sources are safe and supportive of life.

2 MATERIAL & METHODS

To construct the sensor, conductive ink was formulated and optimized using 810 mg of graphite (GR) as the conductive component, 5 mg of sodium alginate (SA) as a binder, and 2.5 mL of ultrapure water to adjust the ink's viscosity. An adhesive mask was applied to a pre-sanded and cleaned PET substrate, outlining the areas for the working, auxiliary, and reference electrodes. These regions were then filled with the GR-SA conductive ink and applied using a spatula. The assembled sensors were subsequently dried at 50 °C for 30 minutes in an oven.

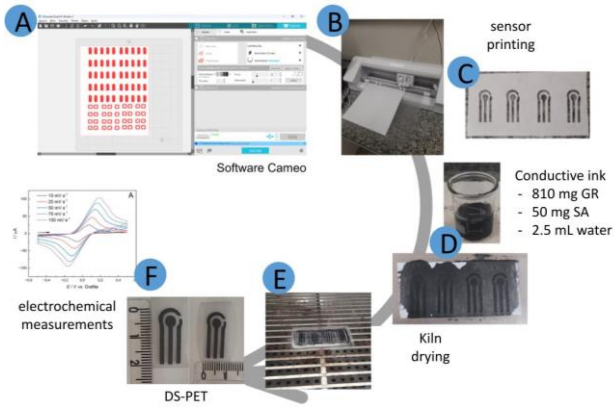

Figure 1 Schematic representation of the DS-PET manufacturing process. A) Design of sensors in software. B) Cut out the adhesive mask with a cutting printer. C) Laying mask on PET substrate. D) Manufacture of condura ink and application to PET. E) Drying of sensors for paint adhesion. F) Voltammetric experiments..

After the initial drying, the sensor was modified using biochar (BC) materials synthesized and donated by Prof. Dr. Mohini Sain from the University of Toronto, Canada, to the Nanotechnology and Electroanalysis Laboratory (LEN, Portuguese acronym). This was combined with copper nanoparticles (CuNPs) to create a BC-CuNPs suspension. First, 40 mg of BC was suspended in ethanol and sonicated for 15 minutes to ensure homogeneity. Then, 16 mg of sodium dodecyl sulfate (SDS) was added as a surfactant, and the mixture was sonicated for an additional 15 minutes. For the reduction of CuNPs, 26 mg of sodium borohydride ($NaBH_4$) was introduced, and the suspension was sonicated further for 30 minutes. Subsequently, an ethanolic solution containing 12 mg of $CuCl_2$ was gradually added to the suspension under stirring. The resulting composite was centrifuged at 3200 rpm for 5 minutes, washed with ethanol, and dried in an oven at 60ºC for 24 hours. 10 µL of this suspension was then applied to the working electrode of the disposable sensors, which were dried again at 50°C for 30 minutes. Following this, the sensors underwent characterization through Field Emission Gun Scanning Electron Microscopy (FEG-SEM), Energy Dispersive X-ray Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), and electrochemical analysis using Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV). After these processes, the sensors were used for detecting methylparaben.

3 RESULTS & DISCUSSION

The electrochemical behavior of the DS-PET sensor was analyzed using Cyclic Voltammetry (CV) within a potential range of -0.5 to +0.5 V in a 0.2 mol L^{-1} PBS solution (pH 7.0), containing 5.0 mmol L^{-1} of the redox couple $[Fe(CN_6)]^{3-/4-}$. Scanning speeds varied from 10, 25, 50, 75 and 100 mV s^{-1}. The sensor exhibited excellent reversibility and clear resolution in the oxidation and reduction peaks, showing significant increases in these peaks with changes in scanning speed, as illustrated in Figure 2A. Additionally, there was a progressive and linear escalation in the currents for the redox process, correlating with the scanning speed, depicted in the Anodic Peak Current/Cathodic Peak Current vs. the square root of scan-rate (I_{pa} / I_{pc} *vs.* $v^{1/2}$) graph in Figure 2B. These findings highlight a good adhesion of the conductive ink to the PET substrate and demonstrate its robust electrochemical performance.

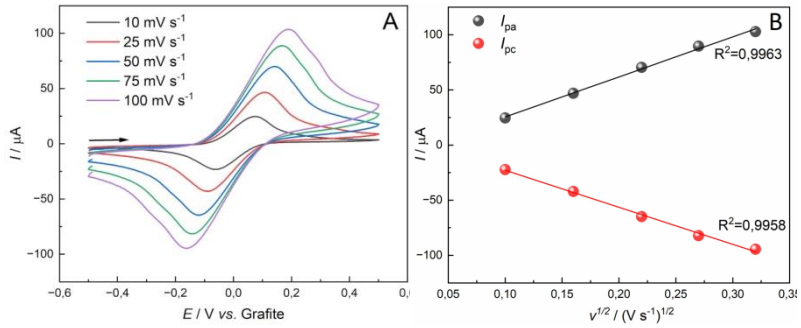

Figure 2 - A) Cyclic voltammograms obtained with the DS-PET sensor in a 0.2 mol L^{-1} PBS solution (pH 7.4) containing 0.1 mol L^{-1} of KCl and 5.0 mmol L^{-1} of the redox couple $[Fe(CN_6)]^{3-/4-}$, for scan-rate of 10, 25, 50, 75 and 100 mV s^{-1}. B) Graph I vs. $v^{1/2}$.

The voltammogram depicted by the black line in Figure 3A illustrates the DS-PET sensor's voltammetric response in a 0.2 mol L^{-1} PBS solution (pH 7.0), where no analyte is present. Conversely, the presence of 10 mmol L^{-1} methylparaben (MP) is shown by the red voltammogram, which indicates an oxidation process at an Anodic Peak Potential (E_{pa}) of +835.1 mV *vs.* Graphite. Figure 3B details this electro-oxidation process, characterized by the irreversible release of an electron and a proton from the MP molecule, leading to the absence of a corresponding reduction peak.

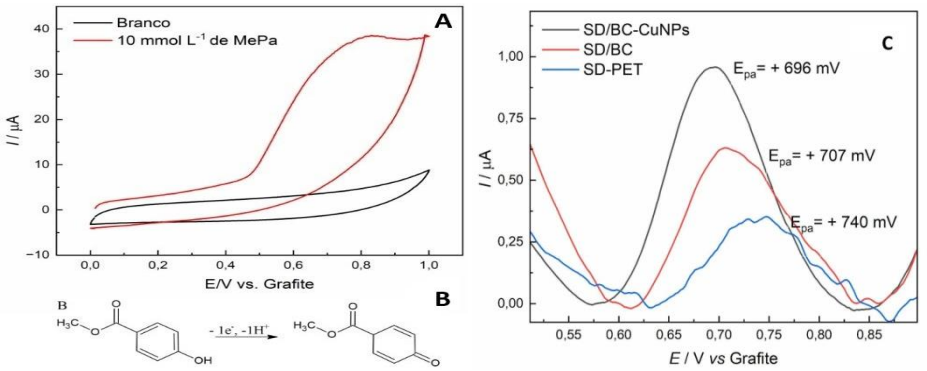

Figure 3 - A) Cyclic voltammograms of the DS-PET sensor in the absence (black line) and presence (red line) of 10 mmol L^{-1} MP in 0.1 mol L^{-1} PBS (pH 7.0), v = 90 mV s^{-1}. (Analysis volume: 100µL). B) Electro-oxidation of MP. C) LSV voltammogram for comparison between DS-PET (blue), DS/BC (red), and DS-PET/BC-CuNPs (black) sensors in the presence of 0.01 mol L^{-1} of MP in 0.1 mol L^{-1} of PBS (pH 7.0), *v* = 90 mV s^{-1}. (Analysis volume: 100µL).

Further investigations into the electrochemical behavior of MP on the DS-PET electrode used Cyclic Voltammetry (CV) at a scan rate of 90 mV s^{-1} in a 0.1 mol L^{-1} PBS (pH 7.0) containing 0.01 mol L^{-1} MP. These results, also shown in Figure 3A, confirmed the absence of electrochemical activity without the analyte (black line). However, with 10 mmol L^{-1} MP present (red line), an irreversible oxidation peak occurred at E_{pa} = +835.1 mV *vs.* Graphite. To enhance the peak current of the MP oxidation process, the sensor was modified with biochar (BC) and copper nanoparticles (BC-CuNPs). These modifications were evaluated using Linear Sweep Voltammetry (LSV) in the same buffer solution. As depicted in Figure 3C, the unmodified sensor (blue curve) exhibited an oxidation process at E_{pa} = +740 mV and an anodic peak current (I_{pa}) of 0.34 µA. After modification with BC (red curve), the oxidation occurred at a reduced Epa of +707 mV with an increased I_{pa} of 0.63 µA. Modification with BC-CuNPs (black curve) further reduced the E_{pa} to +696 mV and increased the I_{pa} to 0.96 µA, demonstrating a decrease of 44 mV in the anodic peak potential and a 2.82-fold increase in Ipa relative to the unmodified sensor. Comparatively, the sensor modified solely with BC showed a 33 mV reduction in anodic peak potential and a 1.85-fold increase in Ipa. These enhancements confirm that the addition of BC and BC-CuNPs significantly improves the voltammetric response for MP detection.

4 CONCLUSION

The DS-PET/BC-CuNPs sensor displayed the strongest voltammetric response for electro-oxidizing 10 mmol L^{-1} methylparaben, with an E_{pa} of +835.1 mV *vs.* Graphite and a 2.86-fold increase in I_{pa} compared to the unmodified sensor. These findings highlight significant enhancements in electron transport and sensor sensitivity.

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