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Biochar copper nanocomposite modified sensor for the green electroanalytical sensing of paraquat

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Abstract

Paraquat (PQ) is a widely used herbicide categorized as an environmental contaminant due to its high toxicity and risk to aquatic ecosystems and human health. In this study, we developed a Screen-printed Disposable Polyethylene Terephthalate (SD-PET) sensor using a green sodium alginate/graphite conductive ink. To maximize performance, the electrode surface was modified with a bamboo biochar composite incorporating copper nanoparticles (BC-CuNPs). Under optimized differential pulse voltammetry (DPV) conditions, the BC-CuNPs sensor outperformed the other configurations, displaying excellent linearity for PQ detection from 10 to 250 $\mu\text{mol L}^{-1}$ ($R^2 = 0.988$), a sensitivity of 0.0234 $\mu\text{A } \mu\text{mol}^{-1} \text{ L}$, and limits of detection (LOD) and quantification (LOQ) of 7.65 $\mu\text{mol L}^{-1}$ and 25.48 $\mu\text{mol L}^{-1}$, respectively. Selectivity studies against common aquatic interferents (chloroquine, levofloxacin, and sulfamethoxazole) and tap water assays indicated mild matrix effects, though the device successfully quantified the analyte under competitive conditions. UV-Vis spectrophotometry validated the accuracy of the proposed method as an independent reference technique. Furthermore, the environmental sustainability of the device was quantitatively confirmed by green chemistry metrics, achieving a high AGREE score of 0.71 and a favorable ComplexGAPI profile. Despite presenting a limited shelf life over 21 days, the developed SD-PET/BC-CuNPs sensor stands out as a highly efficient, eco-friendly, and viable alternative for on-site environmental monitoring of paraquat.

Keywords Disposable sensor, Green conductive ink, Bamboo biochar, Copper nanoparticles, Paraquat, Green chemistry metrics

1 Introduction

The increasing presence of emerging contaminants (ECs) in aquatic ecosystems has become a global environmental concern. These substances, which include a vast array of chemicals and microorganisms, are typically not regulated or commonly monitored, yet they are frequently detected at low concentrations in soil, water, and air [1, 2]. The lack of stringent legislation combined with their potential risks to biodiversity and human health underscores the urgent need for efficient monitoring strategies. Among these



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contaminants, Paraquat (PQ), a widely used herbicide in agriculture for weed control, stands out due to its high toxicity [3]. Exposure to PQ is linked to severe tissue damage [4], pulmonary fibrosis [3], and Parkinson's disease [5], besides posing long-term risks through biomagnification in the food chain [6].

The development of technologies for monitoring PQ aligns with the United Nations Sustainable Development Goals (SDGs), specifically SDG 6 (Clean Water and Sanitation) and SDG 14 (Life Below Water). Developing countries, such as Brazil, have committed to these targets, seeking to protect ecosystems and ensure public health through the identification of contamination hotspots. In this context, electrochemical sensors have emerged as a superior alternative to traditional analytical methods like spectrophotometry and chromatography. These devices offer significant advantages, including low cost, rapid analysis, potential for miniaturization, and high sensitivity, enabling in situ environmental monitoring [7, 8]. Such sensors have already demonstrated versatility across various fields, from real-time precision agriculture [9] to the detection of pharmaceuticals [8, 10], pathogens like SARS-CoV-2 [11], and pesticides in food and water bodies [12–14].

The performance of electrochemical sensors is heavily dependent on the materials used for electrode modification. Biochar (BC), a solid material derived from the thermochemical conversion of biomass under oxygen-limited conditions, has gained prominence due to its unique properties, such as high surface area, porosity, and stability [15–18]. The physicochemical characteristics of BC are directly influenced by the biomass precursor and carbonization conditions, allowing it to act as a highly efficient and sustainable electrode modifier [3, 16]. To further enhance its electroanalytical properties, the incorporation of metallic nanoparticles has been widely explored.

Copper nanoparticles (CuNPs), in particular, are excellent modifiers for carbon-based materials due to their synergistic effects, high conductivity, and lower toxicity compared to noble metals. Furthermore, CuNPs are cost-effective and easy to manipulate, contributing to significantly lower limits of detection and increased sensitivity in the identification of molecules such as dopamine and chloroquine phosphate [5, 7, 10].

This work proposes the development of low-cost, disposable electrochemical sensors fabricated from recycled PET and a sustainable sodium alginate/graphite conductive ink. By modifying these sensors with a biochar-copper nanoparticle (BC-CuNPs) composite, we aim to provide a rapid, simple, and efficient analytical tool for PQ detection in natural water. This approach not only democratizes environmental chemistry but also provides a sustainable technological solution for safeguarding water resources.

2 Methodology

2.1 Instrumentation

Morphological and compositional characterizations of the Screen-printed Disposable Polyethylene Terephthalate (SD-PET) sensors were performed via FEG-SEM and EDS using an FEI dual-beam FIB microscope (IQ-UNESP, Araraquara, Brazil). Particle size distribution was determined using ImageJ software, while functional groups were analyzed by FTIR (PerkinElmer Spectrum Two) with a DTGS detector. The environmental profile of the proposed analytical method was evaluated using the complementary AGREE and ComplexGAPI tools, enabling a comprehensive assessment of its greenness, operational aspects, and potential limitations. For practical field deployment, spent

disposable sensors were collected on-site in sealed solid hazardous waste containers and were returned to centralized facilities for controlled high-temperature incineration, preventing environmental dispersion. The overall environmental footprint of the analytical workflow was quantitatively assessed using AGREE and ComplexGAPI metrics, confirming its low environmental impact.

Electrochemical measurements were conducted on a Metrohm Autolab PGSTAT128N (NOVA 2.1 software) using the fabricated SD-PET three-electrode setup (working, auxiliary, and graphite reference). Initial characterization was performed via CV in 0.1 mol L⁻¹ CaCl₂ containing 5.0 mmol L⁻¹ [Fe(CN)₆]^{3-/4-}. Paraquat (PQ) detection was carried out by DPV in pH 4.0 acetate buffer (0.05 mol L⁻¹ CaCl₂) under optimized conditions: 30 s accumulation, -0.2 V cleaning potential (vs. graphite), -25 mV step potential, 100 mV modulation amplitude, 40 mV s⁻¹ scan rate, and a scan range from 0 to -1.5 V.

2.2 Chemicals

Ultrapure water (resistivity ≥ 18 MΩ·cm⁻¹), obtained from a Elga purification system, was used for the preparation of all solutions. Only analytical-grade reagents were employed, with no additional purification steps. The following compounds were used in this study: Paraquat dichloride hydrate PESTANAL®, analytical standard (CAS No: 75365-73-0), sodium acetate (CH₃COONa), acetic acid (CH₃COOH), copper chloride (CuCl₂), sodium hydroxide (NaOH) and ethanol. Additionally, Levofloxacin, Sulfamethoxazol and Chloroquine were included in the interference studies. All reagents were obtained from Sigma-Aldrich (São Paulo, Brazil).

2.3 Fabrication of screen-printed disposable polyethylene terephthalate (SD-PET)

For the fabrication of the disposable devices, adhesive masks were produced using a Silhouette Cameo 4 cutting plotter operated via Silhouette Studio™ software. The resulting adhesive films served as stencils, which were applied onto a previously sanded and cleaned PET substrate to delimit the regions for the working, auxiliary, and reference electrodes. Concurrently, a previously optimized carbon-based conductive ink was formulated by mixing 810 mg of graphite (GR) as the conductive component, 50 mg of sodium alginate (SA) as the biopolymer binder, and 2.5 mL of ultrapure water to achieve the desired viscosity. The Schematic flowchart illustrating the step-by-step fabrication of the disposable sensors is shown in Fig. 1.

The GR-SA ink was manually spread over the adhesive mask using a blade/spatula to fill the delimited electrode areas. After drying in an oven at 50 °C for 24 h to promote complete ink fixation, the bare SD-PET sensors were obtained. Finally, the working electrode surface was modified via drop-casting with the BC-CuNPs suspension to yield the target SD-PET/BC-CuNPs sensors, which were subsequently used for the electrochemical detection of paraquat.

2.4 Synthesis of biochar-copper based nanocomposites

The bamboo-derived biochar (BC), kindly provided by Prof. Mohini (University of Toronto, Canada), was obtained from *Phyllostachys heterocycla* pyrolyzed at 900 °C for 60 min (30 °C min⁻¹), pulverized, and dried at 105 °C overnight. The BC-CuNPs suspension was synthesized by dispersing 40 mg of BC in ethanol via probe-type ultrasonication for 15 min. Subsequently, 16 mg of sodium dodecyl sulfate (SDS) was incorporated



Fig. 1 Schematic flowchart illustrating the step-by-step fabrication of the disposable sensors: from the preparation of the PET substrate and adhesive masks, through the formulation of the graphite/sodium alginate conductive ink, to the manual screen-printing process, final surface modification with the BC-CuNPs composite via drop-casting, and the resulting DPV sensing profile for paraquat

as a surfactant; the vessel was hermetically sealed with laboratory sealing film to preclude solvent evaporation and subjected to an additional 15 min of ultrasonication. For the reduction of CuNPs, 26 mg of the reducing agent sodium borohydride (NaBH_4) was added, and the sealed suspension was placed in an ultrasonic bath for 30 min [19]. To incorporate the nanoparticles, an ethanolic solution containing 12 mg of CuCl_2 was gradually added to the suspension under magnetic stirring. The resulting composite was centrifuged at 3200 rpm for 5 min, washed with ethanol, and dried in an oven at 60°C for 24 h.

For comparison, the described synthesis was also performed without the reduction and incorporation steps to obtain isolated BC, and a separate synthesis was prepared containing only CuNPs. These nanocomposites were suspended in ultrapure water at a concentration of 2.0 mg mL^{-1} and subjected to probe sonication for 5 min to ensure dispersion homogeneity. Finally, $5\text{ }\mu\text{L}$ of the suspension was applied via drop-casting onto the working electrode of the disposable sensors, which were then dried in an oven at 50°C for 30 min.

3 Results and discussion

3.1 Morphological and structural characterization of the SD-PET sensors

To provide a comprehensive understanding of the sensor's performance, the morphology of the conductive ink applied to the PET substrate was investigated via FEG-SEM. Figure 2A–C reveal excellent adhesion between the conductive ink and the substrate, which is attributed to the manual application process. For the sensor modified with BC-CuNPs (Fig. 2D and E), the surface exhibited an irregular morphology with heterogeneous clusters, a characteristic feature of graphite dispersion and the spatula-coating method. Although non-uniform, this morphology is advantageous as it increases the active surface area, thereby enhancing the sensor's sensitivity by facilitating electrochemical reactions [20].

The EDS elemental analysis of the SD-PET/BC-CuNPs sensor surface (Fig. 2F) revealed a composition predominantly consisting of carbon (79.8 wt%), originating from the porous biochar matrix. The spectrum displays a major peak at 0.28 keV corresponding to the C K_α emission line, accompanied by the O K_α line at 0.52 keV (14.0 wt%).

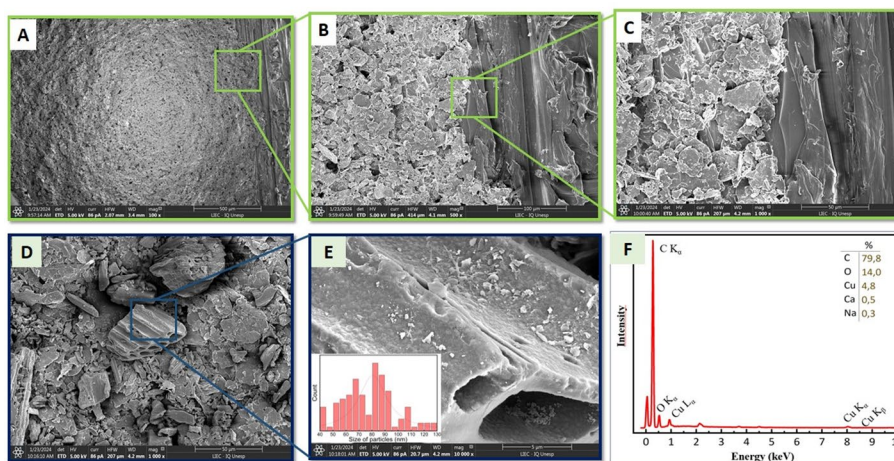


Fig. 2 FEG-SEM images and EDS analysis of the SD-PET sensors. **A** Overview of the SD-PET sensor at 100x magnification. **B** Interface between the conductive ink and the PET substrate (1000 $\times$). **C** Microstructural detail of the manually applied conductive ink. **D** Surface of the SD-PET sensor modified with BC-CuNPs (500 $\times$). **E** Magnified region of the same sensor highlighting heterogeneous clusters (1000 $\times$) (inset: histogram of CuNPs). **F** EDS spectrum of the SD-PET/BC-CuNPs sensor surface, displaying the characteristic X-ray emission lines for carbon (C K_{α}), oxygen (O K_{α}), and copper (Cu L_{α} , Cu K_{α} and Cu K_{β}). Inset: elemental composition (wt%)

successful incorporation of copper (4.8 wt%) was confirmed by its characteristic X-ray emission lines, including the Cu L_{α} at 0.93 keV, alongside the high-energy Cu K_{α} and Cu K_{β} lines at 8.04 keV and 8.90 keV, respectively. The effective dispersion of CuNPs over the biochar support provides an expanded electroactive surface area, directly contributing to the overall enhancement of the sensor's electrochemical response.

3.2 .

FTIR spectroscopy was used to characterize the chemical composition of the materials by analyzing the characteristic vibrations resulting from infrared radiation interacting with the samples, which provides information on molecular structure and identifies functional groups. As shown in Figure S1, the black curve for commercial GR lacks significant bands. The red curve (sodium alginate, SA) shows bands at 3310 cm^{-1} (O–H), 2917 cm^{-1} (C–H), 1600 cm^{-1} and 1410 cm^{-1} (carboxylic bond, O=C–O–), and 1027 cm^{-1} (C–O stretching), consistent with the literature. The blue curve, representing the GR-SA ink, exhibits a transposition of the GR (black) and SA (red) curves, confirming the effective combination of GR and SA in the conductive ink formulation, as evidenced by the FTIR analysis.

3.3 Electrochemical characterization

The electrochemical behavior of the SD-PET sensor was further investigated by cyclic voltammetry (CV) using the ferri/ferrocyanide redox probe ($[\text{Fe}(\text{CN})_6]^{3-/4-}$), as shown in Fig. 3A. The scan rate was varied from 10 to 100 mV s^{-1} , and a gradual increase in both anodic and cathodic peak currents was observed with increasing scan rate. As shown in Fig. 3B, the peak currents exhibited a linear relationship with the square root of the scan rate ($v^{1/2}$), indicating that the electrochemical response of the redox probe at the SD-PET sensor surface is mainly governed by a diffusion-controlled process [21]. The peak-to-peak potential separation ($\Delta E_p > 100 \text{ mV}$) reflects a quasi-reversible electron transfer process for the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe. This is characteristic of disposable

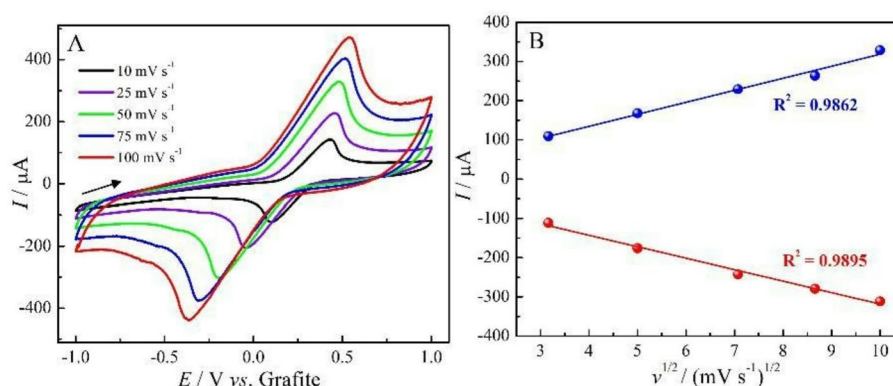


Fig. 3 **A** Cyclic voltammograms recorded with the SD-PET sensor in 0.1 mol L⁻¹ CaCl₂ containing 5.0 mmol L⁻¹ $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as the redox probe, at scan rates of 10, 25, 50, 75, and 100 mV s⁻¹. **B** Plot of peak current as a function of the square root of the scan rate

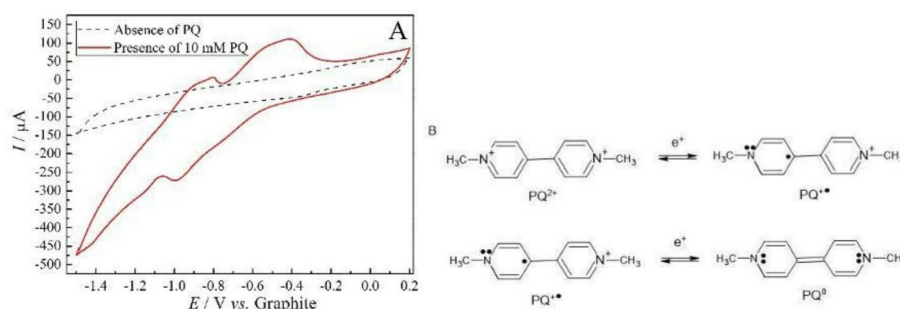


Fig. 4 **A** Cyclic voltammograms recorded with the SD-PET sensor in the absence (black dotted line) and presence (red solid line) of 10 mmol L⁻¹ PQ in 0.1 mol L⁻¹ CaCl₂ at $v = 25$ mV s⁻¹. Analytical volume: 200 μL. **B** Electro-oxidation mechanism of PQ

green-ink electrodes, where uncompensated resistance arises from the non-conductive biopolymer binder (sodium alginate) and the low-temperature curing of the printed SD-PET substrate.

Furthermore, the electrochemical behavior of Paraquat (PQ) at the SD-PET sensor was investigated via cyclic voltammetry (CV). As illustrated in Fig. 4A, no electrochemical activity was observed in the absence of the analyte; however, the addition of 10 mmol L⁻¹ PQ showed two distinct oxidation peaks at $E_{\text{pa}} = -801.8$ mV and $E_{\text{pa}} = -406.3$ mV, alongside a primary reduction peak at $E_{\text{pc}} = -997.1$ mV (vs. graphite). This profile highlights a two-step quasi-reversible mechanism coupled with surface adsorption (Fig. 4B), rather than an ideal Nernstian process. The cathodic scan involves the sequential one-electron reduction of the dication to the radical cation ($\text{PQ}^{2+} + e^- \rightleftharpoons \text{PQ}^{+\bullet}$), followed by the reduction to the neutral species ($\text{PQ}^{+\bullet} + e^- \rightleftharpoons \text{PQ}^0$). While the second step often appears as a broadened shoulder in CV due to slow kinetics and background interference, Differential Pulse Voltammetry (DPV) effectively resolves both reduction steps ($E_{\text{pc1}} = -0.406$ V and $E_{\text{pc2}} = -0.801$ V) by suppressing capacitive charging currents. During the reverse anodic scan, the emergence of two oxidation peaks reflects the re-oxidation of both diffusing and surface-confined species, as the neutral PQ^0 interacts strongly with the hydrophobic bamboo biochar matrix [22–24].

Table 1 Optimized parameters for the construction of the response curve

Parameters	Optimized value
Pulse amplitude	0.1 V
Supporting electrolyte	0.1 mol L ⁻¹ acetate buffer pH 4.0
Potential range	0.0 V a –1.5 V
Cleaning potential	–0.2 V
Preconcentration time	30 s
Scan rate	40 mV s ⁻¹

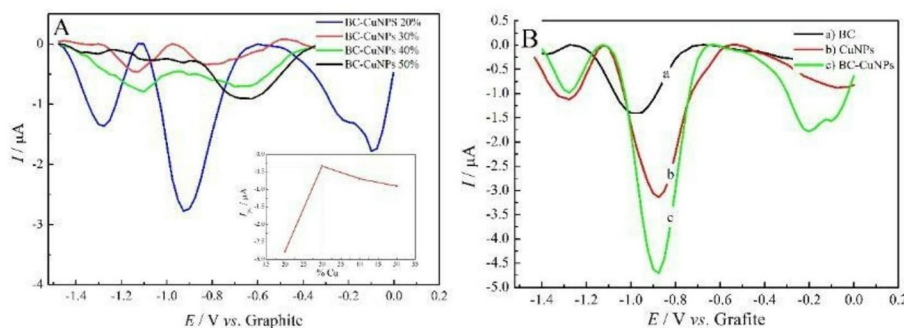


Fig. 5 Optimization and comparative electrochemical performance of the modified sensors for paraquat (PQ) detection. **A** DPV responses for different BC-CuNPs composite percentages (20%, 30%, 40%, and 50% w/w), with the inset showing the peak current (I_{pc}) profile as a function of Cu content; **B** DPV comparison of the SD-PET sensors modified with: (a) BC, (b) CuNPs, and (c) BC-CuNPs (20%). Conditions: 500 $\mu\text{mol L}^{-1}$ PQ in 0.1 mol L⁻¹ acetate buffer (pH 4.0) containing 0.05 mol L⁻¹ of CaCl₂. DPV parameters: pulse amplitude = 100 mV, scan range = 0.0 to –1.5 V, cleaning potential = –0.2 V, accumulation time = 30 s

3.4 Electrochemical behavior of bare SD-PET and SD-PET modified with BC-CuNPs

Following the fabrication of the SD-PET sensor, its electrochemical performance was assessed. To enhance the analytical capability of the SD-PET/BC-CuNPs sensor for paraquat (PQ) detection, key experimental and instrumental parameters were systematically optimized using differential pulse voltammetry (DPV). This optimization process included evaluating the copper content (Cu%) within the BC-CuNPs composite, the scan rate, pulse amplitude, preconcentration potential, and preconcentration time.

The supporting electrolyte pH was optimized for Paraquat (PQ) detection across the 4.0–7.0 range using 0.1 mol L⁻¹ acetate buffer. pH 4.0 was selected for subsequent studies due to superior signal stability, peak reproducibility, and baseline definition. Analytical measurements were conducted with 500 $\mu\text{mol L}^{-1}$ PQ in 0.1 mol L⁻¹ acetate buffer (pH 4.0) and 0.05 mol L⁻¹ CaCl₂. Additionally, scan rates were evaluated from 10 to 75 mV s⁻¹; however, 40 mV s⁻¹ was selected to ensure consistent and reproducible results. Table 1 summarizes these optimized experimental parameters.

The voltammetric behavior of the modified devices was first evaluated to optimize the composition of the sensing platform. To achieve this, the BC-CuNPs composite was prepared at different copper proportions (20%, 30%, 40%, and 50% w/w) relative to the biochar matrix, and their performances were assessed via differential pulse voltammetry (DPV) for the detection of 500 $\mu\text{mol L}^{-1}$ paraquat (PQ). As demonstrated in Fig. 5A, the configuration containing 20% CuNPs yielded the sharpest and most intense reduction peak, establishing it as the optimal composition for the subsequent steps of this study. At higher loadings (30–50% w/w), a decrease in peak intensity and slight peak broadening were observed. Based on the electrochemical response, this trend is likely related to

mass transport constraints and potential nanoparticle agglomeration at higher concentrations, which may reduce the effective electroactive surface area and partially block the accessible adsorption sites of the biochar matrix.

Using these optimized conditions, the performance of the fully modified device was compared against its individual components. Figure 5B illustrates the DPV responses for the three evaluated sensor configurations: SD-PET/BC (curve a), SD-PET/CuNPs (curve b), and SD-PET/BC-CuNPs (20%) (curve c). The configuration modified with isolated biochar yielded a discrete cathodic peak current I_{pc} of $-1.40 \mu\text{A}$. Upon modification with CuNPs alone, the signal reached $-3.1 \mu\text{A}$, which can be attributed to the catalytic properties of the metallic nanoparticles. Remarkably, the synergistic combination in the SD-PET/BC-CuNPs (20%) configuration exhibited the highest current response, reaching an I_{pc} of $-4.8 \mu\text{A}$. This significant increase in signal magnitude represents a 243% enhancement compared to the individual components, underscoring the effective role of copper nanoparticles in improving electron transfer kinetics combined with the excellent adsorptive support provided by the porous biochar matrix.

Remarkably, the synergistic combination in the SD-PET/BC-CuNPs (20%) configuration exhibited the highest current response at $500 \mu\text{mol L}^{-1}$, reaching an I_{pc} of $-4.8 \mu\text{A}$. This represents a 243% enhancement compared to the isolated biochar modifier ($-1.40 \mu\text{A}$), underscoring the vital role of copper nanoparticles in overcoming the intrinsic electrical resistance of raw biochar and accelerating electron transfer kinetics across the porous matrix.

3.5 Analytical performance: calibration curves for different sensors

To evaluate the electroanalytical capability of the developed devices and confirm the advantages of the surface modification, calibration curves for paraquat (PQ) were constructed using three distinct sensor configurations: bare SD-PET, SD-PET/BC, and SD-PET/BC-CuNPs. Figure 6A, B, and C display the differential pulse voltammetric (DPV) responses alongside their respective analytical curves for each optimization stage.

The limit of detection (LOD) and limit of quantification (LOQ) were calculated in accordance with IUPAC guidelines using the equations $\text{LOD} = 3.3 \times s_b / S$ and $\text{LOQ} = 10 \times s_b / S$, where s_b represents the standard deviation of 10 independent measurements of the blank solution (supporting electrolyte under optimal DPV parameters) and S is the slope of the linear calibration plot.

The unmodified SD-PET sensor (Fig. 6A) was first evaluated within a PQ concentration range of $10\text{--}250 \mu\text{mol L}^{-1}$ ($n = 8$). Voltammograms showed a progressive increase in cathodic peak current (I_{pc}) with increasing PQ concentration. From $50 \mu\text{mol L}^{-1}$, a second reduction peak was observed, diminishing possible additional electrochemical processes at higher concentrations. The unmodified sensor demonstrated a sensitivity of $0.0233 \mu\text{A } \mu\text{mol}^{-1} \text{L}$, with a limit of detection (LOD) of 7.95 and a limit of quantification (LOQ) of $26.50 \mu\text{mol L}^{-1}$.

$$I_{pc} (\mu\text{A}) = 0.0068 (\mu\text{A}) - 0.0233 (\mu\text{A } \mu\text{mol}^{-1} \text{L}) \times C_{PQ} (\mu\text{mol} \cdot \text{L}^{-1}) (n = 8) \quad (1)$$

Modification of the electrode surface with bamboo-derived biochar (BC) led to a significant improvement in the peak current, both in terms of magnitude and definition, across the same concentration range (Fig. 6B). This enhanced performance is attributed

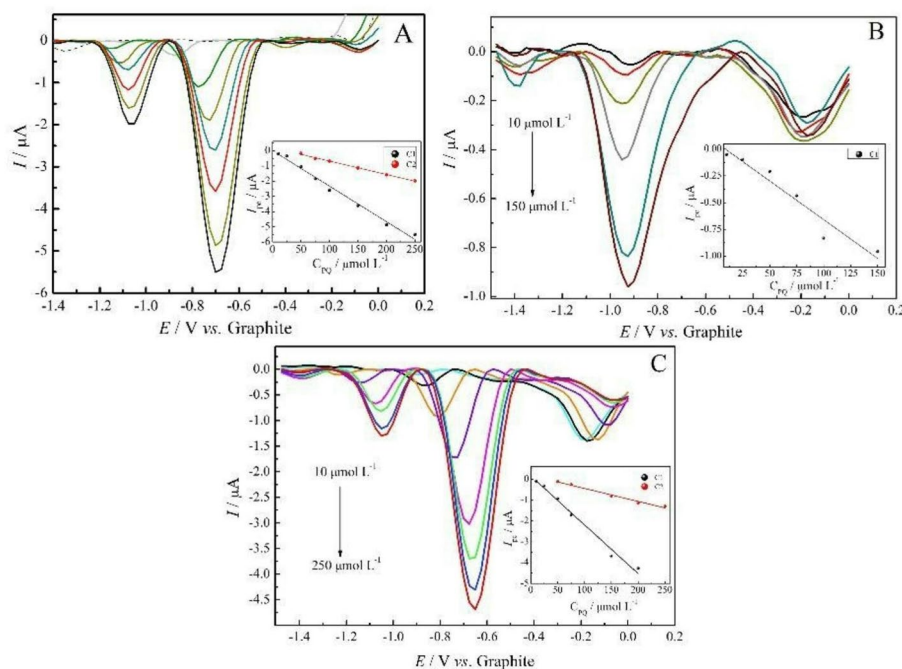


Fig. 6 Differential pulse voltammetric (DPV) responses and corresponding linear calibration curves for paraquat reduction at different optimization stages: **A** Bare SD-PET; **B** SD-PET modified with biochar (SD-PET/BC); and **C** SD-PET modified with the biochar-copper nanoparticle composite (SD-PET/BC-CuNPs). Supporting electrolyte: 0.1 mol L⁻¹ acetate buffer (pH 4.0) containing 0.05 mol L⁻¹ of CaCl₂. DPV conditions: pulse amplitude = 0.1 V, potential range from 0.0 to -1.5 V, cleaning potential = -0.2 V, pre-concentration time = 30 s

to the BC matrix's highly porous structure and the presence of oxygenated functional groups, which facilitate analyte accumulation on the sensor surface. The BC-modified sensor demonstrated a sensitivity of 0.0072 $\mu\text{A } \mu\text{mol}^{-1} \text{ L}$, with a limit of detection (LOD) of 10.02 and a limit of quantification (LOQ) of 33.39 $\mu\text{mol L}^{-1}$.

$$I_{\text{pc}} (\mu\text{A}) = 0.064 (\mu\text{A}) - 0.0072 (\mu\text{A } \mu\text{mol}^{-1} \text{ L}) \times C_{\text{PQ}} (\mu\text{mol} \cdot \text{L}^{-1}) (n = 6) \quad (2)$$

Remarkably, the best electroanalytical performance was achieved with the synergistic platform composed of both biochar and copper nanoparticles (Fig. 6). The SD-PET/BC-CuNPs sensor not only significantly amplified the current responses but also provided the sharpest peak definitions, leading to an outstanding sensitivity of 0.0234 $\mu\text{A } \mu\text{mol}^{-1} \text{ L}$ and a wide linear range from 10 to 250 $\mu\text{mol L}^{-1}$ ($R^2 = 0.988$).

$$I_{\text{pc}} (\mu\text{A}) = 0.1599 (\mu\text{A}) - 0.0234 (\mu\text{A } \mu\text{mol}^{-1} \text{ L}) \times C_{\text{PQ}} (\mu\text{mol} \cdot \text{L}^{-1}) (n = 6) \quad (3)$$

A critical comparison of the calibration parameters reveals distinct electrochemical behaviors among the three configurations. Modification with raw biochar (SD-PET/BC) resulted in a lower slope (0.0072 $\mu\text{A } \mu\text{mol}^{-1} \text{ L}$), which can be attributed to partial blocking of conductive sites by oxygenated functional groups and contact resistance within the raw carbonaceous matrix. Interestingly, while the SD-PET/BC-CuNPs sensor (0.0234 $\mu\text{A } \mu\text{mol}^{-1} \text{ L}$ and the bare SD-PET sensor (0.0233 $\mu\text{A } \mu\text{mol}^{-1} \text{ L}$) exhibited statistically equivalent sensitivities within the lower concentration range (10–250 $\mu\text{mol L}^{-1}$), the nanocomposite modification provided significant operational advantages. First, the unmodified SD-PET sensor displayed peak broadening and secondary electrochemical

responses at concentrations above $50 \mu\text{mol L}^{-1}$, complicating baseline determination. Conversely, the BC-CuNPs platform maintained sharp, single-peak voltammetric profiles with improved signal-to-noise ratios. Second, the nanocomposite expanded the effective active surface area, preventing early surface saturation and electrode passivation at higher analyte levels ($500 \mu\text{mol L}^{-1}$), while yielding marginally superior detection ($7.65 \mu\text{mol L}^{-1}$) and quantification ($25.48 \mu\text{mol L}^{-1}$) limits, this results are summarized in Table 2.

Statistical evaluation of the regression slopes via two-tailed t-tests confirmed that the incorporation of copper nanoparticles into the biochar matrix significantly improves sensitivity relative to the raw biochar modifier ($t_{\text{calc}} = 10.05 > t_{\text{crit}} = 2.306$, $p < 0.0001$). Conversely, comparison between the bare SD-PET and SD-PET/BC-CuNPs sensors revealed statistically equivalent slopes within the $10\text{--}250 \mu\text{mol L}^{-1}$ regime ($t_{\text{calc}} = 0.0795$, $p = 0.9382$). These statistical findings confirm that the primary role of the BC-CuNPs composite is to stabilize the voltammetric response, suppress peak splitting, and extend the linear dynamic range without electrode passivation.

A comparative overview between the proposed SD-PET/BC-CuNPs electrode and other previously reported electrochemical sensors for Paraquat screening is summarized in Table 3. The comparison encompasses key analytical features including the electrode platform, electrochemical technique, linear dynamic range, limit of detection (LOD), and real sample applications.

As observed, conventional solid-state electrodes (e.g., BDDE, GCE) and highly complex nanostructured architectures involving molecularly imprinted polymers or noble metal nanoclusters (such as MIP-AuNC-CS) achieve low nanomolar to femtomolar detection limits. However, these platforms generally require multi-step chemical synthesis, sophisticated surface functionalization, and mechanical polishing protocols between runs, limiting their deployment for rapid point-of-need screening.

Conversely, when comparing the proposed platform with other low-cost or 3D-printed devices (e.g., Gpt-PLA), the SD-PET/BC-CuNPs sensor provides a competitive linear working range and satisfactory analytical performance using differential pulse voltammetry (DPV). Most importantly, it combines simple drop-casting modification, sustainable biochar support, mass-production scalability on flexible PET substrates, and single-use applicability without requiring tedious surface restoration.

3.6 Comparative methodology by UV–Vis spectrophotometry and tap water analysis

The developed electroanalytical methodology for paraquat (PQ) detection using unmodified and modified disposable screen-printed PET electrodes (SD-PET/BC and SD-PET/BC-CuNPs) was validated and compared using complementary UV–Vis spectrophotometry, a technique known for its high sensitivity and broad application in aqueous organic compound quantification. Initial UV–Vis spectra showed a maximum absorbance peak (λ_{max}) at 256 nm, consistent with literature values (257–258 nm). However, this

Table 2 Analytical and statistical parameters for paraquat detection ($10\text{--}250 \mu\text{mol L}^{-1}$) using bare and modified SD-PET sensors

Sensor	Equation ($I_{\text{pc}}/\mu\text{A}$, $C/\mu\text{mol L}^{-1}$)	Sensitivity ($\mu\text{A } \mu\text{mol}^{-1} \text{ L}$)	R^2	LOD ($\mu\text{mol L}^{-1}$)	LOQ ($\mu\text{mol L}^{-1}$)
Bare SD-PET (n=8)	$I_{\text{pc}} = 0.00684\text{--}0.02331 \text{ C}$	0.02331	0.98756	7.95	26.50
SD-PET/BC (n=6)	$I_{\text{pc}} = 0.06405\text{--}0.00723 \text{ C}$	0.00723	0.92326	10.02	33.39
SD-PET/BC-CuNPs (n=6)	$I_{\text{pc}} = 0.15994\text{--}0.02345 \text{ C}$	0.02345	0.98431	7.65	25.48

Table 3 Comparison of the analytical performance of the developed SD-PET/BC-CuNPs sensor with other reported electrochemical sensors for Paraquat determination

Sensor	Type	LOD	Samples / matrix	Ref.
^a Bare BDDE	Conventional	1.5 nmol L ⁻¹	natural water, tea, fruit juice	[25]
^b MWCNT/DHP-GCE	Conventional	1.0e-8 M	Natural water	[26]
^c PPY-g-NGE	Conventional	58 nmol L ⁻¹	Ground water and Lake water	[27]
^d Boron-doped carbon nanowall electrode	Conventional	0.47 μmol L ⁻¹	Tap water	[28]
^e ZnCo ₂ O ₄ /C ₃ N ₅	Conventional	7.6 nmol L ⁻¹	food samples	[29]
^f MIP-AuNC-CS	Conventional	2.3 fmol L ⁻¹	water and food	[30]
^g Gpt-PLA 3D printed electrode	Conductive filament 3D printed sensor	0.01 μmol L ⁻¹	Honey samples, water samples and food samples	[31]
SD-PET/BC-CuNPs	SPE	7.65 μmol L ⁻¹	Tap water	This work

^aBare Boron-Doped Diamond Electrode, ^bMulti-Walled Carbon Nanotube / Dihexadecyl Phosphate modified Glassy Carbon Electrode, ^cPolypyrrole-grafted Nitrogen-doped Graphene Electrode, ^dBoron-Doped Carbon Nanowall Electrode, ^eZinc Cobalt Oxide / Nitrogen-rich Carbon Nitride, ^fMolecularly Imprinted Polymer—Gold Nanocluster—Chitosan, ^ggraphite conductive polylactic acid filament (Gpt-PLA)

near-UV region is prone to spectral overlap from various organic compounds, limiting the technique's selectivity in complex environmental matrices, though it is suitable for preliminary validation. Calibration curves, built at 256 nm, exhibited excellent linearity (R^2 0.9955) in both ultrapure and tap water, with similar slopes (0.01632 and 0.01649, respectively), suggesting minimal matrix influence on the PQ spectrophotometric response. These results are shown in Figure S3 of the Supplementary Material.

Comparing the electrochemical results (DPV), the SD-PET/BC-CuNPs sensor showed the best analytical performance, with the highest sensitivity ($0.0234 \mu\text{A } \mu\text{mol}^{-1} \text{ L}$) and the lowest LOD and LOQ (7.65 and $25.48 \mu\text{mol L}^{-1}$). The unmodified sensor had comparable sensitivity ($0.0233 \mu\text{A } \mu\text{mol}^{-1} \text{ L}$) but slightly higher limits. The SD-PET/BC sensor performed the worst (sensitivity: $0.0072 \mu\text{A } \mu\text{mol}^{-1} \text{ L}$; highest limits).

These findings indicate that the inclusion of copper nanoparticles in the BC-CuNPs composite enhances the sensor's electrochemical response, improving charge transfer, sensitivity, and detection limits. While UV–Vis served as a suitable reference technique, the electroanalytical results highlight the potential of the SD-PET/BC-CuNPs sensor for PQ detection in aqueous samples.

The developed Differential Pulse Voltammetry (DPV) methodology, utilizing the SD-PET sensor, was evaluated for its analytical performance by applying it to tap water samples containing paraquat (PQ). To simulate realistic environmental sample conditions, an analytical curve was generated via DPV using the SD-PET sensor in a matrix composed of 25% tap water. The supporting electrolyte consisted of 0.1 mol L⁻¹ acetate buffer pH 4.0 containing 0.05 mol L⁻¹ of CaCl₂ with tap water collected in the laboratory (FCA/UNESP, Botucatu, SP). The linear range was from 50 to 250 μmol L⁻¹, as shown in Figure S4 of the Supplementary Material.

The equation of the line provided, considering the peak of analysis (highest peak) was:

$$I_{pc} (\mu A) = 0.6695 (\mu A) - 0.0162 (\mu A \mu mol^{-1} L) \times C_{PQ} (\mu mol L^{-1}) \quad (4)$$

which has a correlation coefficient $R^2 = 0.994$ ($n = 5$ concentrations).

When comparing the sensitivity obtained in this study, represented by the slope of the analytical curve (0.0162 μA μmol⁻¹ L), with that previously determined in pure supporting electrolyte (0.0233 μA μmol⁻¹ L), a reduction of approximately 30.5% is observed. This result indicates the influence of the matrix effect associated with tap water on the sensor response. This behavior can be attributed to the presence of inorganic ions and dissolved organic substances, which may compete with the analyte for active sites on the electrode surface or affect charge transfer processes at the electrode/solution interface. Despite this reduction in sensitivity, the sensor maintained good linearity and satisfactory analytical response, demonstrating potential for PQ detection under conditions that simulate real environmental samples.

To critically evaluate the practical utility of the proposed SD-PET/BC-CuNPs sensor in environmental monitoring, its analytical performance must be contextualized against established regulatory frameworks. The calculated LOD of 7.65 μmol L⁻¹ (1.97 mg L⁻¹) is substantially higher than the maximum residue limits (MRLs) enforced for drinking water, such as the European Union threshold (0.0001 mg L⁻¹) or the Brazilian CONAMA Resolution 357/2005 guidelines for freshwaters (low μg L⁻¹ range). Consequently, the present sensor is not intended to replace centralized chromatographic techniques (e.g., HPLC–MS/MS) for routine trace-level compliance monitoring of municipal drinking water. Instead, the analytical value of this disposable, eco-friendly platform lies in its potential for decentralized, on-site screening of acute contamination scenarios. In cases such as undiluted agricultural runoff near application fields, industrial effluent discharges, or accidental chemical spills, paraquat concentrations can temporarily reach the mg L⁻¹ regime. Under these conditions, the sensor provides a rapid, low-cost preliminary alert system. Furthermore, integrating this green sensing device with solid-phase extraction (SPE) or magnetic pre-concentration steps represents a viable pathway to bridge the analytical gap toward trace-level (μg L⁻¹) environmental monitoring in future applications.

The dynamic linear range established for the SD-PET/BC-CuNPs sensor (10–250 μmol L⁻¹ corresponding to 2.57–64.3 mg L⁻¹ of paraquat) is well-suited for real-world environmental monitoring. Considering that typical pesticide concentrations in contaminated agricultural runoff or surface waters rarely exceed a few milligrams per liter, an upper limit of 64.3 mg L⁻¹ comfortably encompasses both routine environmental contamination and acute spill scenarios. Higher concentrations (>250 μmol L⁻¹) induce

partial biochar surface saturation and peak splitting due to intermediate adsorption, limiting linearity; however, such elevated levels can be readily analyzed using standard sample dilution protocols.

3.7 Effect of interfering species on paraquat (PQ) electrochemical response and long-term stability

To evaluate the vulnerability of the SD-PET/BC-CuNPs sensor to competitive matrix effects, the cathodic response of $100 \mu\text{mol L}^{-1}$ paraquat was measured in the presence of $50 \mu\text{mol L}^{-1}$ of three representative electroactive pharmaceuticals: levofloxacin (LEV), sulfamethoxazole (SMX), and chloroquine (CLQ). These specific co-contaminants were selected due to their nitrogenous heterocyclic structures and electroactive moieties, which can physically or electrochemically compete with paraquat for active adsorption sites on the biochar-copper composite. As shown in Fig. 7A, the addition of LEV, SMX, and CLQ resulted in notable peak current suppressions ranging from 27 to 36%. This substantial decrease indicates significant competitive inhibition and cross-reactivity at the electrode surface, primarily driven by competitive biochar pore occupancy and partial blocking of active copper nanoparticle sites. Consequently, the sensor cannot be considered fully selective against electroactive organic micropollutants when present at elevated concentrations.

Concurrently, the storage stability of the device was evaluated over time using DPV in the presence of $500 \mu\text{mol L}^{-1}$ PQ. As shown in Fig. 7B, a progressive decline in the cathodic peak current was observed relative to the freshly fabricated sensor. The device exhibited a significant performance drop of 53.3% after 8 days of storage, which further extended to 58.0% and 63.5% after 15 and 21 days, respectively. These findings indicate that the developed sensor possesses a limited shelf life, suggesting that future optimizations should focus on enhancing long-term stability or that the devices are best suited for immediate, single-use on-site screening.

Regarding inorganic matrix constituents (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), their potential interference is mitigated by the fact that simple inorganic ions do not undergo electrochemical reduction within the cathodic potential range applied for paraquat (-0.5 V to -0.9 V). This was corroborated by the acceptable recovery rates obtained in tap water samples (Sect. 3.5). However, natural organic matter (such as humic acids) may interact electrostatically with cationic paraquat species, potentially causing additional signal attenuations in complex surface waters. Therefore, while the proposed sensor serves as

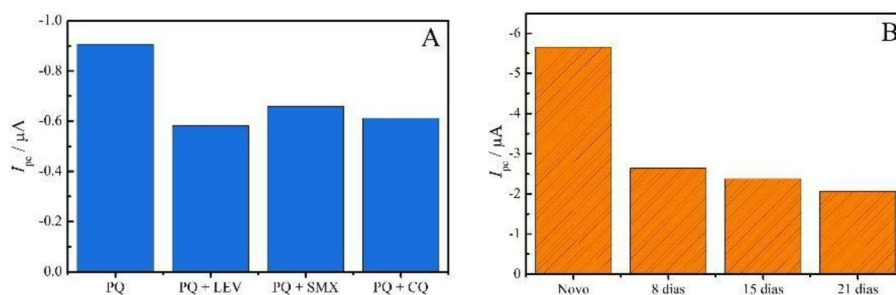


Fig. 7 Selectivity and stability studies of the developed device. **A** Cathodic peak current (I_{pc}) responses for paraquat (PQ) in the absence and presence of potential interfering species (LEV, SMX, and CQ), illustrating matrix competition; **B** Long-term storage stability profile evaluated over 21 days, showcasing the percentage reduction in the analytical signal

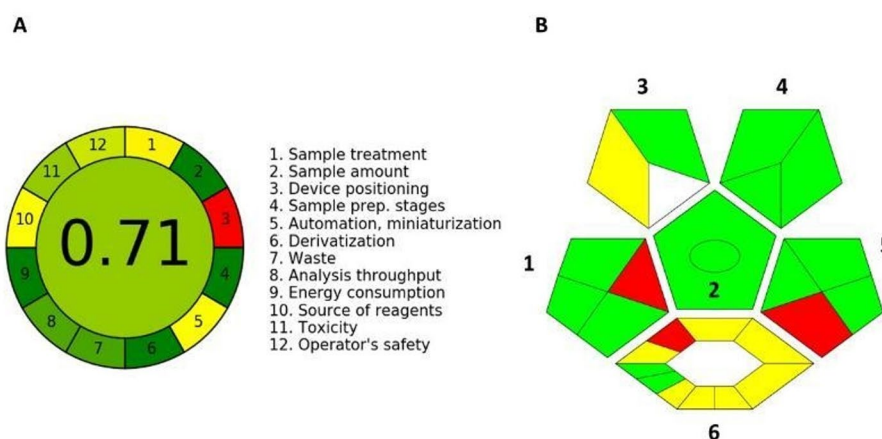


Fig. 8 Greenness and sustainability evaluation of the developed method. **A** AGREE pictogram showing the overall score of 0.71 and its 12 parameters; **B** ComplexGAPI pictogram illustrating the compliance levels for each evaluated requirement

an effective screening tool for typical environmental water matrices, the standard addition method or sample pre-treatment is strictly recommended when analyzing complex effluents containing high organic loads or pharmaceutical co-contaminants.

Storage stability tests over 21 days at 25 °C revealed that the sensor's sensitivity decreases by 53.3% after 8 days, with continued decay thereafter. This performance loss is caused by the atmospheric oxidation of zero-valent copper nanoparticles (Cu^0) into semiconducting copper oxides ($\text{Cu}_2\text{O}/\text{CuO}$), which increases charge-transfer resistance. Given this rapid degradation, the sensors should be prepared shortly before use. For extended shelf life, protective measures such as vacuum packaging.

3.8 Greenness assessment of the proposed electroanalytical method

The greenness profile of the proposed electroanalytical method was evaluated using the AGREE software, a metric based on the 12 principles of Green Analytical Chemistry. This tool provides a comprehensive score ranging from 0 to 1, allowing the overall sustainability of the analytical procedure to be assessed [32]. As shown in Fig. 8, the developed SD-PET/BC-CuNPs sensor achieved an AGREE score of 0.71, indicating a favorable greenness profile and strong adherence to sustainable analytical practices. Scores above 0.60 are generally associated with methodologies presenting good environmental performance [33]. This result reinforces the sustainable character of the proposed approach, which combines the miniaturization of the electroanalytical platform with the use of renewable and bio-based materials, such as biochar, as well as graphite, water, and sodium alginate biopolymer for the preparation of the conductive ink.

Despite the positive AGREE score, some parameters showed lower individual performance, indicating opportunities for further improvement. The main aspects requiring optimization were related to sample treatment (Principle 1), device positioning (Principle 3), automation (Principle 5), and the source of reagents (Principle 10). In the present study, sample handling was classified as an off-line procedure because the water samples were collected, transported, and subsequently analyzed in the laboratory. A prospective scenario was therefore evaluated using the AGREE software, considering that an aliquot would be collected and immediately analyzed at the sampling site using a portable potentiostat, while all other assessment parameters were kept unchanged. Under these

conditions, the overall AGREE score increased from 0.71 to approximately 0.77, corresponding to an estimated relative improvement of approximately 8%. This result indicates that in-field analysis could improve the greenness profile of the method by reducing sample transportation, storage, and manipulation. Nevertheless, the estimated score represents a prospective assessment rather than an experimentally validated improvement, since the analytical performance of the sensor under actual field conditions has not yet been investigated. For ComplexGAPI, no equivalent numerical improvement can be reported because this tool provides a color-coded pictogram rather than a cumulative score. However, in-field measurements would positively affect the fields associated with sample transportation, preservation, and storage. Thus, the use of portable potentiostats could improve both the practical applicability and environmental performance of the proposed method, enabling on-site electrochemical detection of PQ [34, 35]. In addition, the automation of the analytical procedure represents an important opportunity for improvement. Flow-based approaches, such as sequential injection analysis, could be implemented to reduce manual operation, improve analytical frequency, and minimize operator exposure [36, 37]. Another aspect that could be improved is the synthesis route employed for the copper nanoparticles. Although the proposed sensor incorporates more sustainable components, including PET, biochar, graphite, water, and sodium alginate, the CuNPs were synthesized through a conventional chemical route using sodium borohydride. NaBH_4 presents handling and safety concerns because its hydrolysis in aqueous media can be exothermic and generate flammable hydrogen, requiring controlled reaction and waste-management conditions [38], whereas SDS is an anionic surfactant that may cause skin and eye irritation, particularly at higher concentrations or under prolonged exposure [39]. In this context, the biosynthesis of copper nanoparticles using plant extracts or other biological resources could represent a potentially greener alternative, as naturally occurring compounds may simultaneously act as reducing and stabilizing agents [33, 34]. Replacing or reducing the use of NaBH_4 and SDS could improve aspects related to reagent hazard, operator safety, and waste generation. However, the actual environmental benefits of a biogenic route should be confirmed through a direct comparison considering reagent consumption, energy requirements, waste generation, nanoparticle stability, and analytical performance.

The ComplexGAPI assessment complemented the information obtained by AGREE by providing a more detailed visualization of the environmental impact associated with different steps of the procedure, including both the analytical stage and the pre-analysis processes. In region 1, related to sample preparation, the red section was attributed to the off-line sampling approach, indicating that the method could be improved by implementing direct or in-field analysis. Region 2, associated with reagents and solvents used during sample preparation and analysis, presented a yellow section due to the use of supporting electrolyte and reagents in the analytical medium. Although the method is performed in aqueous medium and does not require organic solvents, a more direct strategy, such as the addition of the supporting electrolyte directly into the electrochemical cell followed by sample introduction, could further reduce external sample handling.

In Region 5, the red section was associated with the need for specialized waste management after analysis. Although the proposed method generates only a small amount of liquid waste due to the miniaturized analytical volume, the used disposable sensor must also be considered solid chemical waste, particularly because it may contain adsorbed

PQ residues after the electrochemical measurement. During this study, all used SD-PET/BC-CuNPs sensors, PQ-containing solutions, and other materials that came into contact with paraquat were handled as contaminated chemical waste and were not discarded with ordinary municipal waste. These residues were segregated and stored in designated hazardous-waste containers according to the institutional waste-management procedures of the university. They were subsequently collected by a specialized company contracted by the institution, which was responsible for their appropriate treatment and final disposal. Nevertheless, the need for specialized collection and treatment remains an environmental limitation of the proposed platform and is therefore appropriately represented by the red classification of Region 5 in the ComplexGAPI assessment.

Finally, region 6 of ComplexGAPI corresponds to the pre-analysis processes, in which the fabrication of the SD-PET/BC-CuNPs sensor was considered. This region included the preparation of the conductive ink and the synthesis of CuNPs, which were obtained through a chemical reduction route. The use of sodium borohydride, SDS, and copper chloride contributed to a less favorable classification in this section. Therefore, replacing this synthetic route with a biogenic approach, for example using plant extracts as reducing and stabilizing agents, could significantly improve the greenness of the pre-analysis process. Overall, the combined AGREE and ComplexGAPI results demonstrate that the proposed method presents a favorable sustainability profile, mainly due to miniaturization, low reagent consumption, aqueous medium, and the use of bio-based materials, while also identifying specific aspects that can be optimized in future studies.

To contextualize the AGREE score obtained for the proposed method, its greenness profile was compared with that of a closely related electroanalytical platform previously reported for hydroxychloroquine determination in water samples. The previously developed sensor was based on a glassy carbon electrode modified with flax-shive-derived hydrochar and biosynthesized silver nanoparticles and achieved an AGREE score of 0.68. The score of 0.71 obtained for the present SD-PET/BC-CuNPs platform is therefore within a similar range, indicating a greenness performance comparable to that of another biomass- and metal-nanoparticle-based electroanalytical method. However, the difference between the scores should be interpreted cautiously because the methods involve different target analytes, electrode configurations, material-synthesis routes, sample volumes, and experimental conditions.

ComplexGAPI does not provide a cumulative numerical score; consequently, the two methods were compared according to their color-coded profiles. In the previously reported method, the main unfavorable aspects were associated with off-line sample collection and transportation, the use of the full 5 mL sample volume, and waste generation. The present method also presents limitations related to off-line sample handling and the management of paraquat-contaminated waste. Nevertheless, the miniaturized analytical volume of the proposed platform reduces sample, electrolyte, and liquid-waste consumption. In contrast, the chemical synthesis of CuNPs and the requirement for specialized disposal of the used sensors remain opportunities for further improvement.

Despite the promising performance of the SD-PET/BC-CuNPs sensor for decentralized Paraquat screening, certain practical limitations warrant further investigation. The platform exhibits a constrained shelf life due to the atmospheric oxidation of metallic Cu⁰ to copper oxides (Cu₂O/CuO), resulting in a 53.3% signal attenuation after 8 days, while matrix constituents and co-existing electroactive species cause partial sensitivity

suppression. To overcome these limitations, future work will focus on integrating anti-oxidation protective coatings and molecular imprinting strategies to boost selectivity. Additionally, transitioning toward biogenic green synthesis of CuNPs and coupling the disposable sensor with portable, smartphone-controlled potentiostats will be essential steps to enable fully automated, point-of-need environmental monitoring.

4 Conclusion

This work successfully demonstrated the feasibility of developing sustainable, disposable electrochemical sensors (SD-PET) utilizing recycled PET substrates and a biopolymer-based conductive ink for the reliable detection of paraquat (PQ). The optimized SD-PET/BC-CuNPs configuration exhibited superior analytical performance, providing a wide linear range from 10 to 250 $\mu\text{mol L}^{-1}$ ($R^2 = 0.988$) and a low limit of detection (LOD) of 7.65 $\mu\text{mol L}^{-1}$. The synergistic combination of bamboo-derived biochar and copper nanoparticles effectively enhanced the electron transfer kinetics and expanded the active surface area.

Assays performed in tap water highlighted a typical matrix effect, which reduced the analytical sensitivity from 0.0234 to 0.0162 $\mu\text{A } \mu\text{mol}^{-1} \text{ L}$; nevertheless, the device retained sufficient capability for accurate real-world monitoring. In terms of selectivity, while ubiquitous inorganic ions present in tap water do not compromise analyte detection, electroactive pharmaceutical co-contaminants (LEV, SMX, CLQ) induced a 27–36% signal suppression under competitive stress conditions. This limitation highlights the necessity of utilizing standard addition protocols when applying the sensor to complex environmental samples containing organic micropollutants. Crucially, the greenness and low environmental footprint of the proposed methodology were quantitatively validated by a high AGREE score of 0.71 and a favorable ComplexGAPI profile. Despite a limited shelf life over 21 days, the developed device stands out as a highly promising, eco-friendly, and cost-effective analytical tool for decentralized on-site screening of paraquat in aquatic environments.

Supplementary Information

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Supplementary Material 1

Author contributions

E.Y.I.: Investigation, Methodology, Writing—original draft. F.C.B.: Formal analysis (green chemistry metrics), Writing—review & editing. M.K.L.S.: Conceptualization, Data curation, Visualization, Supervision, Writing—original draft, Writing—review & editing, Project administration. I.C.: Conceptualization, Resources, Supervision, Validation, Writing—review & editing, Funding acquisition.

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Data availability

The datasets generated and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable. This study did not involve human participants or animal subjects. Not applicable. This study did not involve human participants.

Consent for publication

Not applicable. This study did not involve human participants. (ou: All authors have read and approved the final manuscript and give their consent for publication.)

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