

3D-Printed Carbon Black/PLA Electrodes for Detection of Lead and Copper in Water

Nesrine Hakimi¹, Ahmed Zouaoui¹, Rabab Madjour¹

¹ Laboratoire Croissance et Caractérisation de Nouveaux Semiconducteurs (LCCNS),

Faculté de Technologie,

Université Sétif 1 Ferhat Abbas, 19000, Sétif, Algérie.

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ABSTRACT

Three-dimensional (3D) printing has significantly advanced electrochemical sensing by enabling the rapid development of low-cost, customizable sensor platforms. In this work, fused deposition modeling (FDM) was employed to fabricate electrodes composed of carbon black and polylactic acid (CB/PLA) for the electrochemical detection of lead (Pb^{2+}) and copper (Cu^{2+}) in aqueous solutions. A dedicated electrochemical pretreatment process markedly improved electrode sensitivity, yielding detection limits of 10^{-5} M for Pb^{2+} and 10^{-6} M for Cu^{2+} , as determined by cyclic voltammetry. Impedance spectroscopy analysis revealed enhanced electrical conductivity following pretreatment, attributed to increased exposure of electroactive carbon black sites. These 3D-printed electrodes thus represent a sustainable and cost-effective approach for on-site monitoring, offering a practical solution for real-time analysis of heavy metal contaminants in various environmental settings. Future studies will focus on optimizing electrode design and expanding the range of detectable contaminants to enhance applicability in environmental monitoring.

Keywords: Fused Deposition Modeling (FDM), electrochemical sensor, carbon black/PLA composite, lead (Pb^{2+}) detection, copper (Cu^{2+}) detection, environmental monitoring.

INTRODUCTION

Three-dimensional (3D) printing has gained considerable attention in recent years as a versatile and cost-effective manufacturing technique for a wide range of applications, including electrochemistry [1-5]. This technology enables the rapid fabrication of complex and customized geometries with minimal material waste and reduced production costs. In electrochemical systems, 3D-printed components have been extensively employed in energy storage [6, 7], biosensing [8, 9], and more broadly, in the development of integrated electrochemical devices [3, 10-17].

The functionality of 3D-printed electrochemical sensors depends largely on the electrical conductivity of the printed materials. Conductive filaments can be obtained either by blending carbon-based nanomaterials with thermoplastic polymers [13, 18-21] or by post-printing modifications, such as electrodeposition of metallic coatings [22-25]. Alternatively, commercially available conductive filaments, such as polylactic acid (PLA) loaded with carbon black (CB), provide an accessible and reproducible option for producing conductive structures. PLA is a biodegradable polymer widely used in additive manufacturing, while carbon black is a low-cost, nanostructured conductive additive commonly used in polymers [25-27].

Despite these advancements, the application of 3D-printed electrodes in environmental electroanalysis, particularly for the detection of heavy metals in water, remains limited [28, 29]. Monitoring of trace levels of lead (Pb^{2+}) and copper (Cu^{2+}) is of high relevance due to their toxicity and prevalence in industrial effluents and drinking water sources. The development of portable, low-cost sensors capable of simultaneous detection of these contaminants is therefore essential for environmental monitoring and public health [29].

In this work, we report the fabrication of 3D-printed electrodes based on commercial CB/PLA filament using fused deposition modeling (FDM). The electrodes were subjected to an electrochemical pretreatment to enhance their surface properties. Their analytical performance for the simultaneous detection of Pb^{2+} and Cu^{2+} ions was evaluated

by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). To the best of our knowledge, this study represents the first demonstration of CB/PLA-based 3D-printed electrodes for dual heavy metal detection in aqueous media.

EXPERIMENTAL DETAILS

In this study, all electrochemical experiments were performed in a three-electrode cell with volumes of 10 ml and 25 ml. The working electrode is a 3D printed carbon black loaded PLA electrode (1 cm² surface area), a carbon rod was used as an auxiliary electrode, and as a reference, the potential was measured with a saturated calomel electrode (SCE). All electrochemical measurements were carried out at room temperature using a BioLogic SP-300 potentiostat, monitored by a computer using EC-Lab software.

MATERIALS USED

The conductive filament employed for the fabrication of 3D-printed electrodes was Protopasta Conductive PLA, a composite material composed of polylactic acid (PLA) and carbon black, specifically engineered for electrical conductivity. This material was selected due to its suitable compromise between electrical conductivity, mechanical performance, and printability.

The electrical properties of the filament, such as volume resistivity and resistance, as well as the influence of printing parameters on the final printed parts, are summarized in Table 1 below [30].

Table 1. Properties and Printing Parameters of Protopasta Conductive PLA Filament [30]

Property	Specification
Filament Name	Protopasta Conductive PLA
Composition	PLA + Carbon Black
Filament Diameter	1.75 mm
Volume Resistivity (raw filament)	4.8 – 8.4 $\Omega\cdot\text{cm}$
Electrical Resistance (10 cm)	Approximately 2.0 – 3.5 k Ω
Volume Resistivity (printed parts)	14.4 – 33.6 $\Omega\cdot\text{cm}$ (dependent on printing parameters)
Printing Temperature Range	210°C – 230°C
Recommended Nozzle Diameter	≥ 0.4 mm

ELABORATION AND PREPARATION OF THE 3D PRINTED CARBON BLACK/PLA WORKING ELECTRODE

- Printing the Electrodes (Step 1)

The working electrode was fabricated via fused deposition modeling (FDM) using a polylactic acid (PLA) filament composite loaded with carbon black (carbon black/PLA). The electrode geometry, comprising a flat plate with an active surface area of 1 cm², was designed using CAD software and exported in STL format. The file was subsequently processed into G-code using CURA slicing software. 3D printing was carried out with a 0.4 mm nozzle diameter, under optimized conditions: nozzle temperature at 220 °C and bed temperature at 60 °C.

- Polishing of the Electrodes (Step 2)

Prior to each experimental use, the 3D-printed electrodes were polished using wet abrasive paper (first 600 grit, then 1200 grit), moistened with distilled water, until a visually homogeneous surface was achieved. The electrodes were subsequently rinsed thoroughly to remove any residual particles.

- Electrochemical Pretreatment of the 3D-Printed Electrodes (Step 3)

To activate the electrochemical surface and enhance exposure of the conductive carbon black domains within the carbon black/PLA composite, the electrodes underwent an electrochemical pretreatment. A potential of +1.4 V was applied for 200 s, followed by -1.0 V for an additional 200 s, in a 0.05 M NaOH aqueous solution, in accordance with a previously reported procedure [31]. After treatment, the electrodes were rinsed multiple times with distilled water and gently dried using absorbent laboratory paper.

RESULTS AND DISCUSSIONS

BEHAVIOR OF THE CARBON BLACK/PLA ELECTRODE FOR LEAD AND COPPER DETECTION

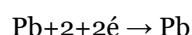
The electrochemical performance of the 3D-printed carbon black/PLA electrode was assessed by investigating its behavior at the electrode/electrolyte interface. This study aimed to evaluate the electrode's ability to detect Pb^{2+} and Cu^{2+} ions through their specific electrochemical properties and to confirm its reliability as a sensing platform.

STUDY BEFORE PRETREATMENT

- Study for Lead

The electrochemical response of Pb^{2+} ions was studied by cyclic voltammetry (CV) using a carbon black/PLA electrode in an aqueous solution containing 0.1 M KCl and 0.01 M PbCl_2 , with a scan rate of 50 mV/s.

The voltammogram (Figure 1) shows a distinct cathodic peak around -1.16 V vs. SCE, corresponding to the reduction of Pb^{2+} to metallic lead, which is deposited on the electrode surface according to the following reaction:



During the reverse scan, a sharp anodic peak is observed at approximately -0.076 V vs. SCE, attributed to the oxidation and dissolution of the previously deposited metallic lead.

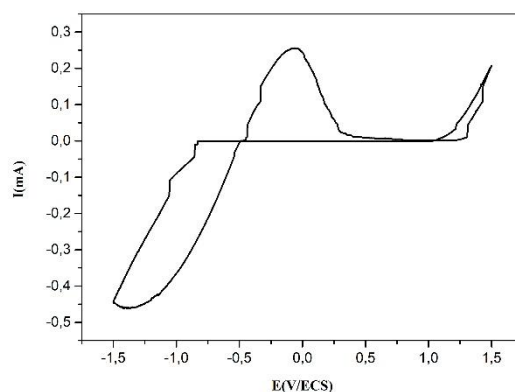
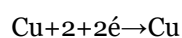


Figure 1: Cyclic voltammogram for a carbon black/PLA electrode in an aqueous solution of 10^{-1} M KCl and 10^{-2} M PbCl_2 at a scan rate of 50 mV/s; before pretreatment.

- Study for Copper

The recorded curve in Figure 2 corresponded to a carbon black/PLA electrode immersed in an aqueous solution of 0.1 M KCl containing 0.01 M CuCl_2 , with a scan rate of 50 mV/s. The cyclic voltammogram obtained was characterized by a reduction peak around -0.759 V vs. SCE, corresponding to the reduction of Cu^{2+} cations to metallic copper, which deposited directly on the working electrode according to the following reaction:



During the anodic scan, two clearly visible oxidation peaks were observed, the first at 0.371 V vs. SCE and the second at 1.03 V vs. SCE, attributed to the successive dissolution processes of the copper previously deposited during the reduction.

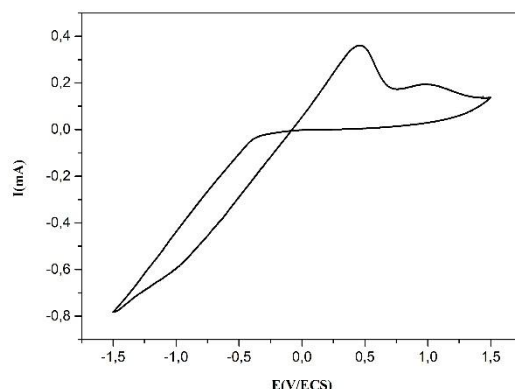


Figure 2: Cyclic voltammogram for a carbon black/PLA electrode in an aqueous solution of 10^{-1} M KCl and 10^{-2} M CuCl_2 at a scan rate of 50 mV/s; before pretreatment.

STUDY AFTER PRETREATMENT

Pretreatment proved to be essential for enhancing both the sensitivity and detection performance of the fabricated electrodes. For the working electrodes produced from carbon black/polylactic acid filaments, an electrochemical activation step was applied to expose the conductive carbon black domains, thereby significantly improving the electrochemical properties of the 3D-printed electrodes.

- Study for Lead

Under the same experimental conditions as previously described, a second voltammetric analysis was carried out using the electrochemically pretreated electrode. The aim was to activate and expose the carbon black sites on the electrode surface and thus enhance its conductivity. The resulting voltammogram exhibited a similar shape to that obtained prior to pretreatment, but with noticeably higher current intensities, indicating improved electron transfer kinetics (Figure 3).

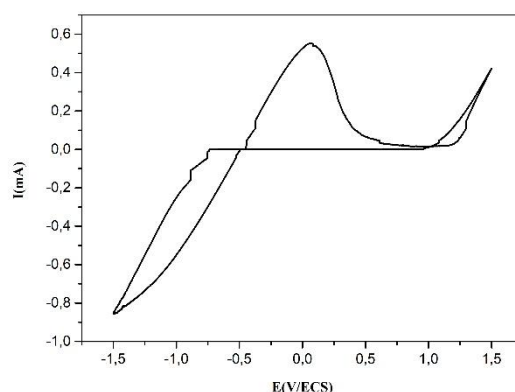


Figure 3: Cyclic voltammogram for a carbon black/PLA electrode in an aqueous solution of 10^{-1} M KCl and 10^{-2} M PbCl_2 at a scan rate of 50 mV/s; after pretreatment.

- Study for Copper

Cyclic voltammetry was then performed under identical conditions to those used for Figure 2, in order to evaluate the electrochemical response of the pretreated electrode and to assess its enhanced conductive properties. As shown in Figure 4, the shape of the voltammogram remained similar to that obtained before pretreatment, but the intensities

of both the oxidation and reduction peaks increased significantly, confirming the improved conductivity of the activated electrode.

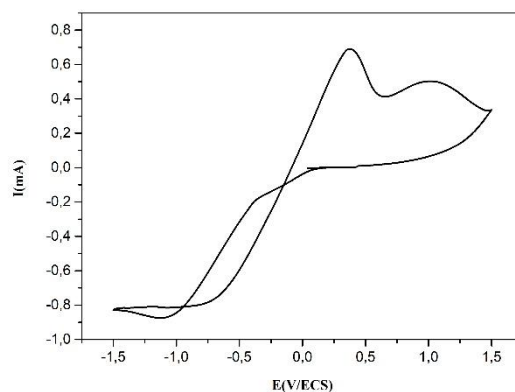


Figure 4: Cyclic voltammogram for a carbon black/PLA electrode in an aqueous solution of 10^{-1}M KCl and 10^{-2}M CuCl_2 at a scan rate of 50 mV/s; after pretreatment.

COMPARATIVE STUDY OF PRETREATED VS. UNTREATED ELECTRODES

In order to evaluate the effectiveness of the electrochemical pretreatment, A comparative analysis was carried out to assess the effect of pretreatment on the electrochemical response of the carbon black/PLA electrode.

- Study for Lead

To better assess the impact of pretreatment on the electrochemical performance of the carbon black/PLA electrode, cyclic voltammograms recorded before and after pretreatment were superimposed. As shown in Figure 5, the oxidation and reduction peak currents for lead were significantly higher following pretreatment. This increase in peak intensity reflected the enhanced electrochemical activity of the exposed carbon black sites, thus confirming the improved sensitivity of the electrode toward lead detection.

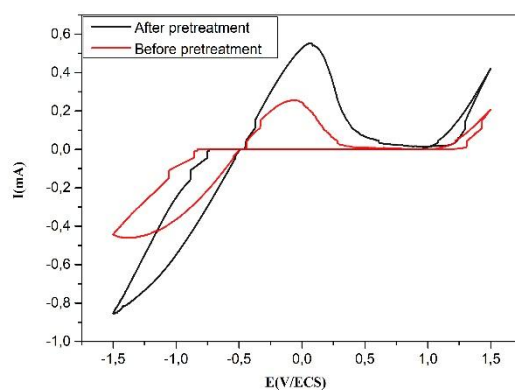


Figure 5: Comparison of Voltammograms from Figure 1 and Figure 3.

- Study for Copper

A similar comparison was performed for copper. The voltammograms obtained before and after pretreatment were analyzed to highlight the effect of electrode activation. As illustrated in Figure 6, the pretreatment process significantly enhanced the oxidation and reduction signals of copper, confirming its critical role in improving both the sensitivity and detection capability of the carbon black/PLA electrode for copper ions.

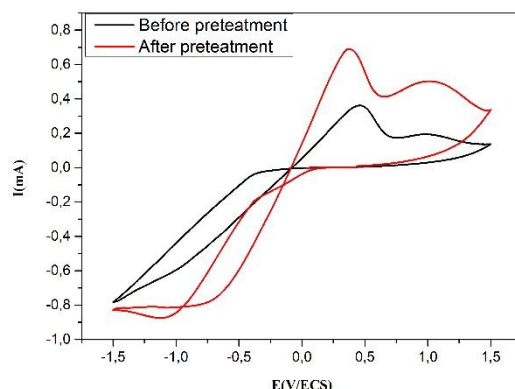


Figure 6: Comparison of Voltammograms from Figure 2 and Figure 5.

EFFECT OF THE CONCENTRATION OF LEAD CATIONS AND CUPRIC CATIONS

To evaluate the sensitivity of the pretreated carbon black/PLA electrode, its electrochemical response was studied at varying concentrations of Pb^{2+} and Cu^{2+} ions using cyclic voltammetry.

- Lead Cations

Figure 7 presents the cyclic voltammograms of a pretreated carbon black/PLA electrode recorded in an aqueous solution of 0.1 M KCl containing different concentrations of PbCl_2 : $C_1 = 10^{-3}$ M, $C_2 = 10^{-4}$ M, and $C_3 = 10^{-5}$ M. As expected, the peak currents associated with the oxidation and reduction of lead increased with increasing Pb^{2+} concentration. Notably, the electrode exhibited a detectable electrochemical response even at a concentration as low as 10^{-5} M, demonstrating its sensitivity toward lead detection at low levels.

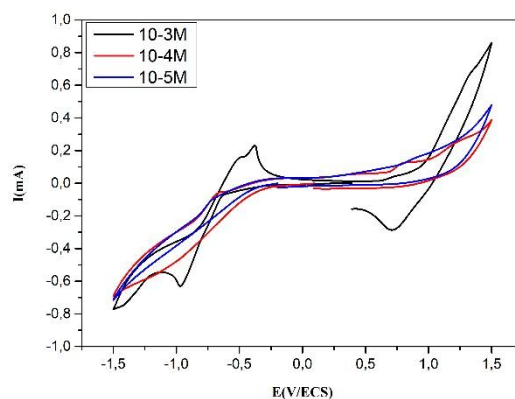


Figure 7: Redox curves of lead on a PLA printed electrode in an aqueous solution of 0.1M KCl obtained at different concentrations of PbCl_2 : $C_1=10^{-3}\text{M}$, $C_2 10^{-4}\text{M}$ and $C_3 10^{-5}\text{M}$, at $v=50\text{mV/s}$.

- Copper Cations

To evaluate the detection capability of the carbon black/PLA electrode for copper ions at low concentrations, cyclic voltammetry was performed in an aqueous solution of 0.1 M KCl containing various concentrations of CuCl_2 : $C_1 = 10^{-4}$ M, $C_2 = 10^{-5}$ M, and $C_3 = 10^{-6}$ M. As shown in Figure 8, the electrode generated clear oxidation signals corresponding to copper even at concentrations as low as 10^{-6} M, confirming its suitability for trace-level copper detection.

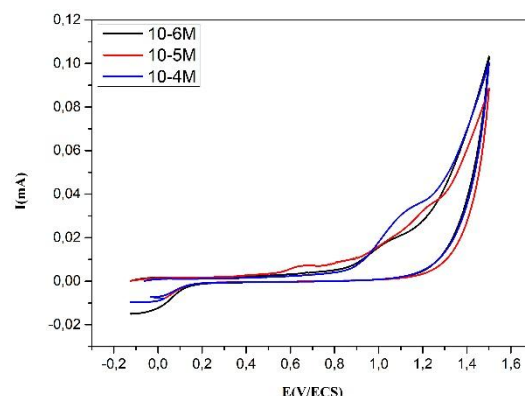


Figure 8: Oxidation curves of copper on a PLA printed electrode in an aqueous solution of 10^{-1}M KCl obtained at different concentrations of CuCl_2 : $C_1=10^{-4}\text{M}$, $C_2=10^{-5}\text{M}$ and $C_3=10^{-6}\text{M}$, at $v=50\text{mV/s}$.

SPECTROSCOPIC STUDY OF THE 3D PRINTED CARBON BLACK/PLA ELECTRODE

To investigate the electrical properties of the 3D-printed carbon black/PLA electrode, electrochemical impedance spectroscopy (EIS) was employed. Measurements were conducted in a 0.1 M KCl aqueous solution over a frequency range from 100 kHz to 10 mHz , at open-circuit potential. Two electrode conditions were compared: before pretreatment (blue curve) and after pretreatment (pink curve).

As illustrated in Figure 9, the Nyquist plots display a semicircular shape at high frequencies, associated with the charge transfer resistance, followed by a linear segment at low frequencies, indicative of a diffusion-controlled process. Notably, the diameter of the semicircle is significantly reduced for the pretreated electrode, reflecting a lower charge transfer resistance and, consequently, enhanced electrical conductivity after electrochemical activation.

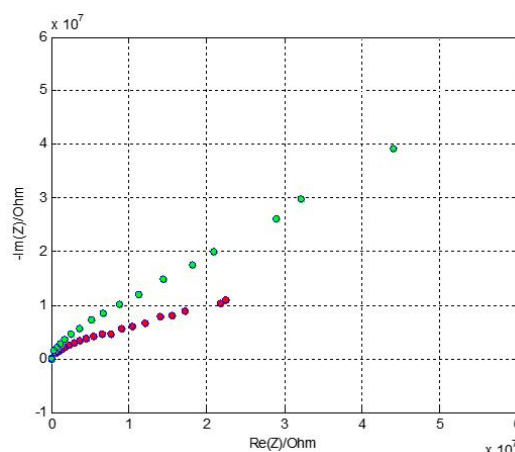


Figure 9: Nyquist diagrams for a carbon black/PLA electrode; over a frequency range between 100 KHz and 10 mHz , in an aqueous solution of 10^{-1} M KCl: (blue): a carbon black/PLA electrode Before pretreatment; (pink): a carbon black/PLA electrode after pretreatment.

CONCLUSION

This study successfully demonstrates the fabrication and electrochemical enhancement of 3D-printed electrodes composed of carbon black and polylactic acid (CB/PLA) for the detection of lead (Pb^{2+}) and copper (Cu^{2+}) in aqueous solutions. The utilization of fused deposition modeling (FDM), a cost-effective 3D printing technique, enabled the creation of customizable electrodes, highlighting the potential of additive manufacturing in electrochemical sensing.

A critical aspect of this research was the implementation of a dedicated electrochemical pretreatment process to optimize the electrodes' performance. This pretreatment, involving the application of specific potentials in a sodium hydroxide solution, proved to be instrumental in significantly enhancing the electrodes' electrical properties. The pretreatment process effectively activates the carbon black component within the PLA matrix, leading to increased exposure of electroactive sites and consequently, improved conductivity.

Electrochemical characterization using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) unequivocally validated the effectiveness of the pretreatment method. CV analysis demonstrated a notable increase in current intensities for both lead and copper detection after pretreatment, indicating enhanced electrochemical activity. EIS measurements further corroborated these findings, revealing a decrease in the semicircle radius in Nyquist plots for pretreated electrodes, confirming the improvement in conductivity.

The optimized electrodes exhibited remarkable sensitivity for the detection of heavy metal ions. Notably, lead ions were detected at concentrations as low as 10^{-5} M, and copper ions were detected down to 10^{-6} M. These detection limits underscore the potential of 3D-printed CB/PLA electrodes as a viable alternative to traditional analytical techniques, offering comparable, and in some cases, superior sensitivity.

The advantages of employing 3D printing for the fabrication of electrochemical sensors are manifold. Additive manufacturing offers the ability to produce complex geometries at reduced costs, enabling rapid prototyping and device customization. The use of conductive filaments, such as carbon black/PLA, further contributes to the sustainability of the sensor development process, as PLA is a biodegradable material.

This research highlights the considerable potential of optimized 3D-printed CB/PLA electrodes for on-site environmental monitoring of heavy metals. The development of portable, cost-effective, and sustainable detection devices based on this technology can address the critical need for water quality control in various settings. This includes industrial applications, where real-time monitoring of heavy metal contaminants is crucial, and resource-limited regions, where access to advanced analytical equipment may be limited.

Future research efforts should focus on further enhancing the performance and applicability of 3D-printed electrochemical sensors. This may involve exploring the optimization of printing parameters to achieve even greater control over the electrodes' properties. Surface functionalization techniques can be investigated to improve the selectivity of the electrodes towards specific target analytes. Furthermore, the integration of these electrodes into complete, automated analytical systems would streamline the monitoring process and facilitate real-time data acquisition.

In conclusion, this study provides a strong foundation for the development of 3D-printed electrochemical sensors for environmental monitoring. The demonstrated enhancement of CB/PLA electrodes through electrochemical pretreatment, coupled with the inherent advantages of additive manufacturing, paves the way for a new generation of portable, cost-effective, and sustainable tools for water quality assessment.

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